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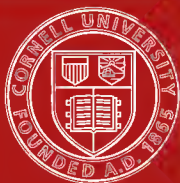
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ENTROPY;
OR,
THERMODYNAMICS FROM AN ENGINEER'S
STANDPOINT.

ENTROPY;
OR,
THERMODYNAMICS FROM AN ENGINEER'S
STANDPOINT,
AND THE
REVERSIBILITY OF THERMODYNAMICS,
BY
JAMES SWINBURNE.

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PREFACE.

My reason for adding another little book on thermodynamics to those in existence is that it is wanted. As far as I am aware there is not any work on the steam- or gas-engine in this country that gives a correct definition of entropy. I do not know about foreign text-books on this subject. This is rather a serious indictment; and when it is added that most treatises on Physics, English and foreign, contain incorrect definitions of entropy, and that even some of those specially on thermodynamics are at fault, especially in classing entropy as a factor of heat, there is no need for any apology, at least, for the appearance of a book like this.

Instead of treating the subject in the orthodox way, however, I have ventured on a new method of explaining it. The reasons for adopting this method are given in the paper, "The Reversibility of Thermodynamics," at the end of the book. This paper was written to be criticised by

those already well up in the subject, and was read before Section A. of the British Association this year, 1903. Though the paper was circulated in proof there was no relevant discussion. It gives a sort of syllabus of the method of exposition adopted in the body of the book, and the reasons for its adoption.

The definition of heat, which makes what is usually denoted by U the heat of the body, is an entirely new departure, as far as I know, though it is quite consistent with the treatment of chemical energy in thermodynamics. If it were not it would be wrong; but its being consistent with correct usage does not mean that it is not new. Another new development is in connection with the entropy temperature diagram. It is assumed in treatises on this subject that the entropy temperature diagram is of the same area as the indicator diagram. The essence of the treatment here followed is that it is not, and that the difference is an indication of the badness of the engine. I am not the first, however, to call attention to the inaccuracies current about the entropy temperature diagram. Marchis ("Comptes Rendus," 132, p. 671) has criticised the ordinary error, and the late Bryan Donkin, in the preface to his translation of

Boulvin's exhaustive book, "The Entropy Diagram," says it "ought only to be applied to reversible cycles"; but he is not at all clear.

The main portion of this book appeared as a series of articles in *Engineering*, August 28th, 1903, and the following issues. I have to thank the proprietors of *Engineering* for permission to republish the articles.

JAMES SWINBURNE.

82, VICTORIA STREET,
WESTMINSTER,
October, 1903.

CONTENTS.



CHAPTER I.

INTRODUCTION.

	PAGE
Origin of Common Error as to Entropy—Personal— Irreversible Changes not Considered Properly .	1

CHAPTER II.

ENTROPY.

Work, Heat, and Waste—What Entropy is Not, and What it Is—Three Kinds of Perpetual Motion— Three Laws of Thermodynamics — Reversible Cycle—Entropy as a Factor of Incurred Waste— Reversibility — Localisation of Entropy — More Convenient Definition of the Entropy of a Body .	6
--	---

CHAPTER III.

THE TEMPERATURE ENTROPY DIAGRAM.

Irreversible or Free Expansion—Difference of Areas of $\theta \phi$ and $p v$ Diagrams—Ungained Work—Dia- gram for Steam—Real Factors of Heat	73
---	----

CONTENTS.

CHAPTER IV.

CONDUCTION.

	PAGE
Movement of Entropy—Conduction of Heat—Volume Growth of Entropy in Conduction—Unit of En- tropy—Physical Meaning of Entropy—Conclusion	94

APPENDIX.

THE REVERSIBILITY OF THERMODYNAMICS.

Present or Orthodox Treatment—Skeleton of Proposed Treatment of Thermodynamics—Waste—Reversi- bility—Equilibrium—Stabilities—Conduction— Units—Conclusion.	113
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ENTROPY ;

OR,

THERMODYNAMICS FROM AN ENGINEER'S STANDPOINT.

CHAPTER I.

INTRODUCTION.

It may be as well to begin by stating that I have no peculiar theories as regards entropy, and that I am merely trying to explain, in as lucid a way as I can, the underlying principle, using the term as it is employed in the thermodynamics of reversible and irreversible changes. The discussion of entropy involves writing a sort of introduction to thermodynamics, so it may be worth while to do so from an engineer's point of view. The treatment of the subject may thus be novel, but novelty is not important; the real aim is to make the theory clear.

Books on thermodynamics do not usually give any idea of any sort of physical meaning of entropy, and only define it so that its magnitude can be

calculated. Many otherwise scientific men, including some engineers, have, unfortunately, got hold of an inaccurate definition of entropy, derived from books which treat exclusively, or almost exclusively, of reversible processes; and as no properly constituted engineer can use mathematical symbols without having an underlying physical idea, a physical interpretation has been forced on to the inaccurate definition, and entropy has been defined as "heat-weight," or as the quantity factor of heat-energy, as if temperature corresponded with head or difference of level, and entropy with weight of water in hydraulics, so that the product of the two, in the case of constant level or temperature, gives energy or heat. Similarly, the entropy temperature is nearly always called a "heat" diagram, whereas its area is not proportional to any particular quantity of existing heat.

In spite of the inaccuracies of thought and statement that are, unfortunately, very common, the $\theta \phi$ diagram is of the utmost value to steam and gas engineers, and my object is to try to get clearer ideas as to the real meaning of the diagram. Neither is the $\theta \phi$ diagram as commonly used seriously wrong. Most writers, after defining entropy incorrectly, unconsciously depart from their definitions in dealing with the $\theta \phi$ diagram, so that the two errors approximately cancel out. There is, however, still an error in the ordinary treatment of

this diagram. But perhaps the chief evil is the confusion of mind into which readers are led by inaccuracy and inconsistency on the part of writers on the steam-engine.

Personal.—As a young man I tried to read thermodynamics, but I always came up against entropy as a brick wall that stopped my further progress. I found the ordinary mathematical explanation, of course, but no sort of physical idea underlying it. No author seemed even to try to give any physical idea. Having in those days great respect for textbooks, I concluded that the physical meaning must be so obvious that it needs no explanation, and that I was especially stupid on that particular subject. (Everyone who studies by himself knows he is particularly stupid in certain directions, and is constantly realising new limitations.) After a few years I would tackle the subject again, and always I was brought up dead by the idea of entropy. I asked people, but I never met any one who could tell me, and I met one, an engineer, who admitted he did not know. Not only could I get no physical idea of entropy, but the definition of entropy, and the statements about it, did not make sense as soon as one tried to understand irreversible changes. Later on, instead of making the common mistake that elementary books are easy to understand, I got into the study of irreversible thermodynamics by the road of physical chemistry, and found that

my previous troubles were due to inaccurate definitions and faulty analogies on the part of writers who had an incomplete grasp of thermodynamics. Having once got accurate and consistent definitions, it is not so difficult to get some sort of physical idea of entropy. I hope I may be pardoned these personal reminiscences ; they are to show that when I write to correct errors in scientific text-books and papers on engineering, written by able men, I do not do so in any spirit of superiority.

Irreversible Changes not Considered.—The source of the whole trouble is the obscurity of the mathematical writer, especially when he is not of the first rank. The early books on thermodynamics, and most of the treatises specially on thermodynamics of the present day, are so anxious to prove the second law with the help of the ideal reversible cycle, and to explain Kelvin's absolute thermometer scale, that they discuss reversible changes almost exclusively, and either neglect irreversible changes, or treat only one case—that of conduction of heat, and that in a meagre way—so that the reader gets quite a wrong notion of the subject. Worse than this, the writer on thermodynamics makes statements which are true of reversible but untrue of irreversible changes, as if they were quite general. The reader who is already acquainted with his subject can mentally insert “in the ideal case of reversibility only,” every here and there, when he studies thermo-

dynamics ; but that there is great confusion on the subject, especially of entropy, is almost entirely the fault of the mathematical writer on thermodynamics. He makes general statements which would only be true in an ideal and impossible case, and makes no attempt to give any physical ideas of the quantities his symbols represent. To an address to the Institution of Electrical Engineers I added a footnote calling attention to the fact that most engineering and physical, as opposed to thermodynamical, writers use a definition of entropy that is numerically accurate in the hypothetical case of reversibility only, and is, in fact, always wrong. I thought merely calling attention to the error and its source would correct it at once, but instead of that it led to an extraordinary correspondence, which astonished me beyond measure by showing that many able men have the most confused notions on the subject. I wrote an article on Entropy in the *Electrical Review* of January 9th, 1903, attempting to give a general explanation so as to cover chemistry as well as physics and engineering ; but the article was written under pressure, and was therefore short, so perhaps it may do no harm to write more fully, dealing with the subject from an engineer's point of view, and discussing the meaning of the θ ϕ diagram. In this way but little of the same ground is covered, and it is always well to approach a subject from two different points of view.

CHAPTER II.

ENTROPY.

Work, Heat, and Waste.—Energy is indestructible ; but it exists in many forms, such as potential, kinetic, electric, magnetic energy on one hand, and heat on the other. All of these, except heat, are interchangeable, with a slight change into heat, which can be diminished, in fact, till very small, and in idea to nothing. All can be changed into heat ; but heat can only be partly changed into the other forms. For want of a better word, and for simplicity, as “ energy ” includes heat, we may call the high-grade energy, such as potential, kinetic, electric, magnetic, &c., “ work,” and low-grade “ heat.” We need not concern ourselves with such things as energy of radiation or chemical energy here. It is the aim of the engineer, when dealing with steam, gas, oil, or compressing engines, to avoid converting or degrading energy into heat. The term “ dissipation of energy ” is generally used to denote degradation of work into heat. As Bertrand points out, the energy is not dissipated, as it is not annihilated—it is degraded, and we may therefore adopt his word, though dissipated does

not really mean annihilated. When work is converted into heat, it may be called "degraded"; but generally some of the heat can be elevated back into work if the rest is given out at a lower temperature. The portion of the heat that must at least be finally given out as heat at the lowest available temperature is of no use: it is waste. I will therefore call the part of the heat that is eventually and unavoidably produced or left at the lowest available temperature the "waste."

The idea of degradation of energy—that is, conversion of work into heat—is quite familiar and clear. Thus all movement against friction means degradation. But there may be a change during which no work is actually converted into heat, but which cannot be unmade, so as to bring the "working substance" back to its original state without involving degradation. Such a change thus "lets us in" for some degradation at some future date, so that the degradation is, as it were, a liability incurred, which must be eventually liquidated.

What Entropy is Not, and What it Is.—In order to get a clear idea as to what entropy is, it is best to begin by stating clearly what it is not. It is not any form of energy, nor a quantity of the dimensions of energy.* It is not heat-weight. It is not

* The misapplication of the term "entropy" by Maxwell and others, with no confusion of idea or inaccuracy of thought, has been corrected long ago, and may be dismissed,

equal to $\int dH/\theta$, as in fact it is essentially greater. It is not heat taken in by the substance divided by the absolute temperature; it is always greater. It is not a factor of heat. It is not, in fact, a function of the heat taken in by the substance. The temperature-entropy diagram is not a heat diagram at all. Its area does not represent the heat of the substance, nor the heat taken in by the substance—it is necessarily greater—nor the energy of the substance, nor the energy taken in by the substance. The statements here contradicted, with others equally misleading, are continually made, not in advanced treatises on thermodynamics, but in books on mathematical physics, and treatises on the steam-engine. If anyone who has not a clear idea of entropy will first banish all preconceived notions as to heat-weight, heat diagrams, or heat divided by temperature, and will think of entropy as the measure of waste actually effected, or inevitably to be effected subsequently, he will have a clear idea. Entropy may be defined thus: Increase of entropy is a quantity which, when multiplied by the lowest available temperature, gives the incurred waste. In other words, the increase of entropy multiplied by the lowest temperature available gives the energy that either has been already irrevocably degraded into heat during the change in question, or must, at least, be degraded into heat in bringing the working substance back to the standard state.

The last part of this definition must not be omitted. The entropy of a body may increase while the entropy of another body that gives it heat decreases equally. In this case there is no increase of entropy of the whole system and no new incurred waste. By increase of entropy here is meant the increase of entropy as a whole in any isolated system, or region, which has no exchange of energy with anything outside it during the increase of entropy. When the increase of entropy of one body is exactly balanced by the corresponding decrease in another, the increase of entropy of the body is called "compensated," and there is no real increase of entropy and no further incurred waste beyond that due to the original production of the entropy. At first sight anyone may say, "if the object is to measure the work irrevocably wasted as heat, why should we not have a quantity of the same dimensions as energy, which would give us the work or heat right off, instead of a quantity like entropy, which is not energy, and has to be multiplied by a temperature to give the energy wasted?" The answer is, that the practical value of heat depends on the temperature, so that unless the lowest available temperature is known, the energy that at least must be run to waste as heat is not known. Suppose by some process, say, 10,000 units of heat were produced at, say, $1,000^{\circ}$ absolute temperature; it does not in the least follow that 10,000 units of work are

wasted as heat, for $1,000^{\circ}$ may not be the lowest available temperature. Suppose 500° is, then, as will be shown directly, half this heat can theoretically be converted back again into work, and $10 \times 500 = 5,000$ units of work are really irrevocably degraded into heat or wasted. Again, if 250° is the lowest available temperature, three-quarters of the 10,000 units can, theoretically, be got back into work, 10×250 being wasted. It is clear, therefore, that the total quantity of work wasted cannot be determined unless we know the lowest temperature available. What we can know, however, is the increase of entropy, a quantity which, when multiplied by the lowest available temperature, gives the work wasted. In this case we might call the entropy 10.

Suppose by some other process a change took place without the actual degradation of work into heat, but of such a nature that to get the substance, for instance, some wire-drawn steam, back into its original state, 10,000 British thermal units would eventually have to be converted into heat; if this heat is given out into a body at a temperature of $1,000^{\circ}$, and 500° is available as a lowest temperature, half can again be theoretically saved, and so on. In this case, however, the increase of entropy takes place when the steam is wire-drawn; its growth is not delayed until the heat is actually produced.

As will be more fully explained directly, we can

only discuss increase of entropy, or decrease of entropy of a body. We cannot evaluate the whole entropy of a body. The entropy of a body is therefore measured by comparison with a standard state. For instance, if water at 32° Fahr. is taken as a standard or zero for water and steam, the entropy of steam is really the difference between its entropy and that of the same weight of water at 32° Fahr.

Three Kinds of Perpetual Motion.—We can certainly take it as a fundamental principle that perpetual motion is impossible. The original idea of perpetual motion was a mechanism that never stopped. It was not necessarily a mechanism that created energy, or gave out energy. We may also take it that energy is conserved, or invariable in quantity. The idea of perpetual motion that involves creation of energy thus contradicts the law of conservation of energy; but a frictionless mechanism, which would run for ever, is merely unrealisable. It is not an absurdity: it is a theoretical abstraction. Every mechanism has friction. But imagine a mechanism in a case through which no energy passes, so that the energy inside the case is constant. Once started, the friction would convert work into heat; but if the mechanism could convert the heat so produced completely into work again, there would be no contradiction of the law of conservation of energy, as the energy is constant.

There would be no stoppage by friction, as all the work converted into heat would be converted into work again, as kinetic energy of motion. We would thus have a form of perpetual motion, not involving frictionless mechanism, and not involving creation of energy. Does this form of perpetual motion rank with the creation of energy form, in which the mechanism gives out work and creates energy; or is it a theoretical abstraction, which cannot be realised only because of the imperfection of our workmanship, like the frictionless mechanism? The answer is that it is not a mere theoretical abstraction, but an absurdity of the same order as the energy-creating form of perpetual motion. It has been called "perpetual motion of the second class." It is perpetual motion which does not involve creation of energy, but involves the opposite or complete undoing of the degradation of energy. The friction degrades work into heat. Some of the heat might be converted back into work if the rest is given out at a still lower temperature; but to make this mechanism work continuously in spite of its friction, all the heat would have to be converted back into work.

The waste may be defined as the residual heat, of which none can be elevated back into work; that is to say, it is the heat that must still remain at the lowest available temperature. Perpetual motion of a mechanism with friction would involve the whole

of the heat produced by friction being elevated back into work. It would thus involve the reduction or diminution of waste once incurred. This abundant experience shows it to be an absurdity of the same order as the creation of energy. We may then say:—

Energy is conservative or constant in quantity in the universe, or in any part of it which neither takes in or gives out energy. This is the first law of thermodynamics, as it involves the equivalence of heat and work.

Waste, once incurred, cannot be diminished in the universe, or in any part of it, which neither takes in nor gives out energy. This is the second law of thermodynamics.

The relations of perpetual motion to thermodynamics may be summed up shortly.

1. Perpetual motion where an otherwise isolated system gives out energy continually is impossible, and not even approximately realisable. This, with the proviso that an otherwise isolated system cannot absorb energy without increasing its internal energy, is the principle of the conservation of energy, or first law of thermodynamics.

2. Perpetual motion of an isolated system, such as a mechanism with friction, is impossible, and not approximately realisable. This is the second law of thermodynamics.

3. Perpetual motion of a frictionless mechanism

is unrealisable. This may be called the third law of thermodynamics.

As every change in existence either involves some friction or some analogous cause of waste, every change or process causes some increase of waste. A change or process which has no friction, and nothing analogous to friction, is an ideal abstraction only, not an absurdity, like the creation of energy, but a useful hypothetical case which can be approximately realised. A frictionless mechanism is the simplest example.

The notion of degradation and of waste is here introduced, not as being convenient for practical use, but as a good way of getting at the significance of entropy. The difficulty with waste is that you cannot give it a value unless you know the lowest available temperature.

Reversible Cycle.—It is shown in text-books that if an imaginary thermodynamic engine, with a perfect gas as working substance, working a Carnot cycle without friction or other cause of waste, takes in heat H_1 from a reservoir or body so large that it can give up this heat without fall of temperature, at temperature θ_1 measured with a perfect gas thermometer, and gives out heat H_2 to another reservoir at θ_2 , the engine returning to its original condition, so that it has performed a cycle, a certain proportion of the heat H_1 will be elevated into work, and the rest must be rejected as H_2 at the lower temperature

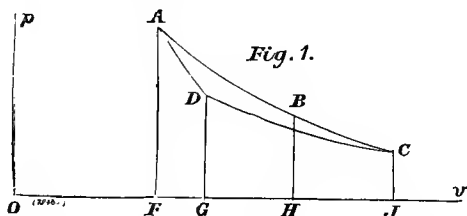
θ_2 , as the engine has, by hypothesis, returned to its original state. It is also shown that $\frac{H_1}{H_2} = \frac{\theta_1}{\theta_2}$ in this particular case.

It must be noticed that H here is not the increase of heat of the gas; it is the decrease of heat of the reservoir; or, to put it more generally, it is the heat that comes into the gas from the outside. This heat may be converted into work at once, so that the heat of the gas is not increased. Again the heat of the gas may be varied without any heat passing in or out through its case or envelope; for instance, by adiabatic compression or expansion.

θ is here the temperature of the envelope the heat H passes through. In reversible changes like this the reservoir and gas are at the same temperature, and so is the envelope, so θ is the temperature of all three. But if the temperature of the working substance and the body that supplies heat H are not uniform, θ denotes the temperature of the surface of the working substance through which the heat passes. This is important, and laxity of statement in books on thermodynamics has given rise to much confusion in this connection. When θ is mentioned hereafter as the temperature of the body, the body and envelope are at the same temperature.

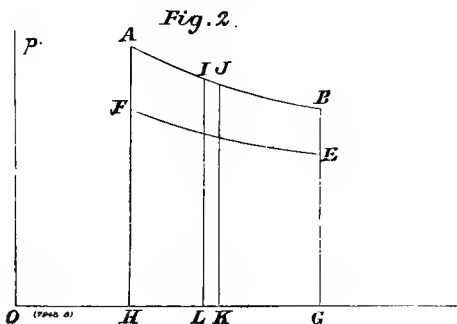
The machine in the ideal cycle with perfect gas,

starting from A, in the $p v$ diagram, Fig. 1, where the gas is at temperature θ , and pressure and volume $p_1 v_1$ takes in heat H_1 , while it slowly expands still at temperature θ_1 . When it has expanded to B, it has thus taken in heat H_1 , and converted it all into external work. The gas has expanded at constant temperature, and Joule's experiment showed that a real gas needs practically no heat to expand it; a perfect gas is supposed to absorb no heat in expansion. From B to C the



gas expands without taking in any heat, and as it does external work its temperature falls to θ_2 . From C to D it is compressed, giving out heat H_2 at temperature θ_2 , and D is chosen so that from it the gas is compressed without giving out any heat until it arrives at A. As the gas has the same internal energy, U_1 , at A and B, and the same, U_2 , at C and D, as it merely changes volume, but not temperature, from A to B, and C to D, the difference between the internal energy of A B and C D is the same, whether the change is by the path B C or

A D. The work done by the gas from B to C is therefore equal to that from A to D. Suppose, therefore, that when the gas has reached B at temperature θ_1 , instead of cooling it by letting it give out its energy as work, we cool it by abstracting heat, without expanding it; it will then fall to E (Fig. 2), as the internal heat energy of a perfect gas varies directly as the temperature. (To make this



quite accurate I have assumed a perfect gas thermometer, whose readings differ very slightly from a mercury instrument.) The height of E will be to that of B as θ_2 is to θ_1 . Now compress the gas to F, giving out heat H_2 ; then give back exactly the heat that was abstracted from B to E, and the temperature rises to θ_1 at A again. It is clear that the height of F is to that of A also as θ_2 is to θ_1 , and that is true of any pressure lines we may draw. Any vertical slice[†] I J K L of the area A B G H is

therefore cut by the curve F E, so that the relation of the whole to the lower part is θ_1/θ_2 , and the ratio of the area A B G H or H_1 to F E G H, or H_2 is as θ_1/θ_2 , and that of A B E F the balance of external work W_b to A B G H or H_1 is $(\theta_1 - \theta_2) \theta_1$, Carnot's ratio. As A B G H is equal to the work done on expansion, and therefore to H_1 , and E F H G to the work put in on compression, given out as H_2 , A B E F is equal to the balance of external work done, or to the heat, $H_1 - H_2$ converted into work. The output of the engine cycle is thus, where W_b is the balance of work done:—

$$W_b = H_1 - H_2 = H_1 \frac{\theta_1 - \theta_2}{\theta_1},$$

and the efficiency

$$\frac{W_b}{H_1} = \frac{\theta_1 - \theta_2}{\theta_1}$$

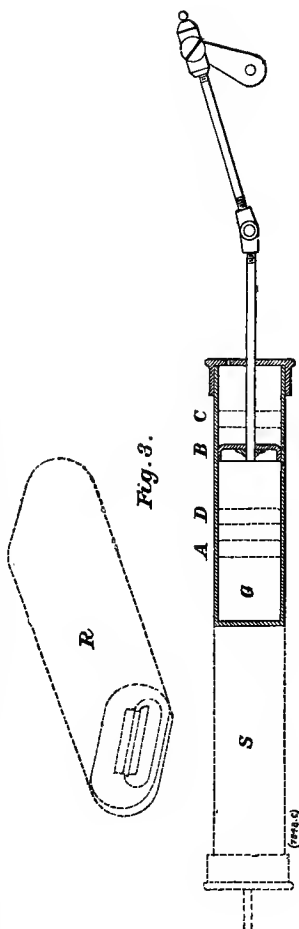
and

$$\frac{H_1}{H_2} = \frac{\theta_1}{\theta_2}.$$

The proof is not conclusive as it stands, because though the heat given out by the gas from B to E is the same as that taken in from F to A, it might be said that the temperatures vary, so that the heat might not be taken in and given out at the same temperature. The lines E B, F A can be divided into a number of equal corresponding parts, each part of E B having a corresponding part of F A. Each pair of parts then represents a corresponding step in temperature due to the same increase or

decrease of heat. A perfect gas thermometer may be made which reads in pressure of gas at constant volume. If the gas in the cylinder is so used, the lines F A and G B would be divided up into θ equal parts, and F A would have $\theta_1 - \theta_2$ equal parts, and so would E B. The heat capacity of a perfect gas being constant, each of these degrees means the same heat taken in at the same temperature.

The proposition can be proved otherwise. Fig. 3 shows a double thermodynamic engine, with two cylinders which may be arranged back to back. The working substance is in the cylinder to the right. First the gas G expands, without using the left-hand engine, at constant temperature, the piston moving from the dotted position A,



to B. Then the heat reservoir R is removed from the cover of the cylinder, and the second cylinder S applied. The gas in S is then slowly expanded, taking heat from the working substance, and also supplying heat of its own. All this heat is converted into work. When the substance is thus cooled to θ_2 , the second cylinder is removed, and a cold reservoir 'applied. The piston is pushed in from B to A, giving out heat H_2 . The other cylinder is then applied, and the gas G heated to its original state by compressing the gas in S to its original state. The double engine has then taken in heat H_1 , and given out H_2 and work W_b , and there is no question about the two intermediate steps. The artist has designed these engines without guides or brasses, because hypothesis prevents there being any friction anyhow.

We have thus one specimen ideal machine which will convert heat from a body at θ_1 into work, rejecting at a lower temperature θ_2 with an efficiency of $\frac{\theta_1 - \theta_2}{\theta_1}$; it is now to be shown that this one specimen will give us information as to the possibilities of all such machines. The machine will obviously work equally well in either direction. If it is reversed, it takes in heat H_2 at the lower temperature, converting it all into work, and takes in more work at θ_1 giving out H_1 . Suppose there were any other possible kind of thermodynamic

engine which could work with a higher efficiency than $\frac{\theta_1 - \theta_2}{\theta_1}$, and suppose it took in H_1 and gave out more balance of work than W_b , say W , and therefore rejected less heat than H_2 , say H_3 ; so that $H_1 - H_3 = W$. Imagine these machines coupled together. The new machine would drive the old one round backwards, as $W > W_b$, and at every turn the hotter reservoir would give as much heat to the new engine as the old engine gave it. But the cooler reservoir would only get H_3 from the new engine every turn, while the old engine would take away H_2 . The difference between W and W_b might then be devoted to overcoming friction, being converted into heat, and given to the lower reservoir. We would then have a case of second-class perpetual motion—namely, a mechanism, with friction, which could be shut up in a case, and go on for ever. The second law of thermodynamics, which, in the form I have put it, is a denial of the possibility of perpetual motion of a machine which has any friction, thus shows that the maximum ideal or theoretical efficiency of a heat engine is $\frac{\theta_1 - \theta_2}{\theta_1}$.

In the example given of a thermodynamic machine with a higher efficiency working the machine of $\frac{\theta_1 - \theta_2}{\theta_1}$ efficiency backwards, we supposed the balance of work per cycle to go into friction. Suppose, however, the friction were reduced a little ;

the pair of engines could take all the heat from the cooler and put it into the hotter reservoir.

Entropy as a Factor of Incurred Waste.—Suppose that we had produced the heat U_1^* by degrading work into heat, say by friction, the heat being produced in a body at temperature θ_1 , and we want to find the waste incurred. If θ_2 is the lowest available temperature, and as the thermodynamic engine is frictionless in its widest sense, so that there is no increase of waste incurred by its working, the incurred waste is, when the heat U_1 is received by the engine as H_1 .

$$H_2 = H_1 \frac{\theta_2}{\theta_1}, \text{ and } \frac{H_2}{\theta_2} = \frac{H_1}{\theta_1}.$$

So that altering the lowest available temperature alters the final waste in proportion. So the incurred waste corresponding to the wasteful conversion of a given quantity of work into an equivalent quantity of heat at any given temperature varies inversely as the temperature at which the heat is formed, and directly as the lowest available temperature. But

* The symbol U is generally used to denote more than mere sensible heat, but it includes sensible heat, and it is used to denote the increment of heat of the body, while H denotes the heat that passes through the envelope. On page 122 it is urged that U should be regarded as the heat of the substance. This involves a new definition of heat, which, though consistent with orthodox thermodynamics, is itself unorthodox. It is, therefore, not introduced here.

the entropy has been defined as a quantity whose increase, when multiplied by the lowest available temperature, gives the inevitable incurred waste. Therefore, still assuming the frictionless thermodynamic engine to be used, the entropy is independent of the lowest available temperature—

as

$$\theta_2 \Phi = H_2$$

by definition,

and

$$\frac{H_2}{\theta_2} = \frac{H_1}{\theta_1}, \Phi = \frac{H_1}{\theta_1},$$

where H is the heat taken in, and θ the temperature of the envelope through which it passes—in this case the same as that of the gas and reservoir. If, therefore, we know the amount of heat U_1 or H_1 produced, and the temperature θ_1 , we can get Φ , and we need not trouble about the ultimate actual waste. Similarly, if a change has taken place which has, in fact, produced no heat, but is of such a nature that to get the working substance, whatever it may be, back to its original state, work must be degraded into heat, we have no information as to the waste so caused. But if we know the highest temperature θ_1 at which the inevitable heat can be given out, we get $H_1/\theta_1 = \Phi$, the entropy; and that gives us the incurred waste corresponding to any lower temperature that may eventually be available. The incurred waste thus varies directly as the lowest available temperature, and directly as the

entropy; and if the lowest temperature is fixed, the waste incurred depends simply on the entropy. If, therefore, a change of any sort involved no increase of entropy, it would involve no increase of waste. Waste can be diminished by obtaining a lower available temperature, but not by any other means. If it were possible, we could then have perpetual motion of the second class, the degradation of work by friction being wholly undone by the mechanism itself. This leads to a most important law; as in all real changes there is either friction, or some analogous source of waste, every change whatever involves waste, small though it may be; and as the change does not affect the lowest available temperature, there is always an increase of entropy. The entropy of the working substance may be increased or diminished or remain constant, but the entropy of the substance and its externals increases. The entropy of an isolated system—that is to say, a system which as a whole neither takes in nor gives out any energy—increases with every change. Entropy once created is therefore permanent for all time. The entropy of the universe tends towards a maximum, and is always growing towards it. Changes take place in Nature in which heat is produced, as by friction. Changes take place in which heat disappears, or is elevated into work, as when a gas expands adiabatically doing external work, or when a photographer dissolves what he calls

hypo in water and gets a mild freezing mixture. In this case the heat is not converted into external work, but into another form of heat. But in Nature no change takes place which does not either produce heat, and thus give rise to waste, or incur waste, without actually producing the heat there and then. Clausius's general statement that the energy of the universe remains constant, and the entropy strives towards a maximum, may therefore be paraphrased thus:—"The energy of the universe is constant, but no change takes place without incurring waste of energy."

It is the business of the engineer to design his machinery to utilise energy to the utmost; and to get as little as possible into the waste form of heat at low temperatures. If he takes care of his entropy, the waste will take care of itself. He should design his steam- or gas-engine so that the original entropy of the fuel and oxygen is increased as little as possible. He is not responsible for the original entropy, but he is for all increase of it; and the more he keeps down the increase of entropy, and the corresponding incurred waste, the more near perfection is his engine.

The theory of thermodynamics is therefore vitally important, and the use of the $\theta \Phi$ diagram should be to the engineer what the balance-sheet is to the financier. The difference is that the financier can make either profit or loss, but the engineer can

only, and must, make loss: it is his business to keep it as small as possible.

Reversibility.—We may now consider the question of reversible and irreversible changes and reversible and irreversible cycles.

If the working substance were to change from the state A to the state B in such a way that the change could be reversed, so that the substance went from B to A in such a way that every part of the change from B to A were exactly the same as the corresponding change from A to B, but in the opposite direction, the change or process would be reversible. There are no reversible changes in Nature; a reversible change is an ideal, or an abstraction, which can only be approximately reached. There is no such thing as a circle or a square or a straight line. They are mathematical abstractions which can be approached, and are exceedingly convenient for reasoning purposes. In a reversible change, not only must the substance retrace exactly the same path, but everything that is involved in the change must retrace the same path. The perfect gas in the thermodynamic engine is the simplest case of reversibility; each of the changes A, B; B, C; C, D; and D, A being reversible. Heat was taken in and work given out from A to B. From B to A, therefore, heat is given out and work taken in, in exactly the reverse way.

When the working substance starts from any

state, and, after change, returns to the original state, it is said to have performed a cycle. If every part of the cycle is made up of changes of which each is reversible, the whole cycle is reversible.

A reversible cycle can cause no incurred waste; for if it did, it would reduce incurred waste if worked the other way, and that would give us second-class perpetual motion. Thus a thermodynamic engine working a reversible cycle might convert a certain quantity of heat H_1 , taken from a reservoir at θ_1 into work W , rejecting H_2 at a lower temperature. If it were coupled to the wasteful reversible engine of a size to give out H_1 at θ_1 , each revolution, that engine, when working backwards, and reducing incurred waste, must take in more than H_2 at the lower temperature to give out H_1 at the highest; so it needs less work each cycle to drive it as $H_2 + W = H_1$. The balance of energy per cycle might then be devoted to overcoming the friction, unavoidable in a real engine, and any balance might do other work, and we would have second-class perpetual motion.

A reversible change is, therefore, a change in which there is no waste incurred, and in a reversible cycle there is no waste incurred.

But we have defined entropy as a quantity whose increase, when multiplied by the lowest available temperature, gives the incurred waste. There is

thus, then, no increase of entropy during a reversible change or a reversible cycle.

The entropy of a working substance may, of course, increase or diminish during a reversible change, but the entropy of an isolated system—that is to say, the working substance—and whatever is affected by the change, remains constant.

Localisation of Entropy.—There has already been incurred an enormous amount of waste in the universe. From the beginning of things there has been degradation of work into heat which can be elevated only partially into work by rejecting some of it at a lower temperature. There is thus an enormous total entropy in the universe, and it is always increasing. More than that, as work gets degraded into heat the lowest available temperature is raised, so that the incurred waste is increasing, not only in proportion to the growth of entropy, but also in proportion to the 'lowest available temperature. But how should entropy be localised? When heat is produced, say, by friction, it means that something gets hotter, or else the heat is absorbed and rendered latent. To get the hotter substance back to its original state it must either give out the heat as heat, or it may expand, doing external work, and cooling to its old temperature, being then compressed to its original volume and rejecting heat, which is degraded energy. The increased waste is clearly connected with the hot

body. The hot body may be moved about, or taken into different surroundings; but to get it back to its original state involves its giving out waste heat. We therefore talk of the entropy of the substance. If the substance is homogeneous in every way, it may be divided up into parts, say seven, and each part will have to give out one-seventh of the waste heat that the whole has to give out in returning to its original state. Entropy is thus additive, like weight, or mass, or volume—not qualitative, like temperature, hardness, or pressure; two tons of water at a given temperature has twice the entropy of one ton, and so on. We thus talk of the entropy of a substance—for instance, the entropy of 17 lb. of steam under given pressure, and volume, and temperature. We can also talk of the entropy per unit mass, or specific entropy of a body. For instance, in working $\theta \phi$ diagrams, the diagram is generally drawn for a pound of steam, and then shows the specific entropy. The term “specific entropy” is not often used, but it is as well to adopt it, to distinguish between the entropy of a mass of steam and its entropy per pound. The example of Professor Planck may well be followed. He uses capitals for volume, entropy, and so on, and small letters for specific volume, and entropy.

It has been shown that during any reversible change there is no incurred waste, and therefore no increase of entropy in the system concerned. Thus,

if an isolated system consists of some heat reservoirs, a perfect gas-engine, and a flywheel; if there is a reversible change, there is no increase of entropy of the system. The perfect gas may have its entropy increased, however, but in that case the entropy of some of the reservoirs is decreased by exactly the same amount.

More Convenient Definition of the Entropy of a Body.—So far we have nearly always discussed the entropy, or the increase of entropy, of a whole isolated system. In thermodynamics this course is inconvenient, and it is much more useful to discuss the entropy of the working substance alone. When the entropy of the working substance is increased by exactly the amount the entropy of the rest of the isolated system is diminished, the increase is called “compensated.” If the working substance increases its entropy by any reversible change, then its increase of entropy is compensated by exactly equal decrease of entropy in other things which are involved in the change. Thus if there were two bodies, say vessels of partly melted lead, A and B, and A were able, through an infinitesimal difference of temperature, to communicate one thermal unit to B, in an infinite time, the change would be sensibly reversible, so the entropy of A and B together would be unchanged.

But if we now proceed to reduce B to the temperature of ice, so as to compare it with the standard

state, the first thing it does is to allow the extra lead thawed by the unit of heat to solidify, giving out a thermal unit at the temperature of melting lead, and the waste corresponding to this unit of heat, divided by the lowest available temperature, was the increase of entropy of B. It has already been explained that this is equal to the heat taken in at the melting-point of lead, divided at the absolute temperature at which it is taken in—namely, $1/\theta$ of a unit of entropy, where θ is the melting-point of lead. The entropy is thus localised.

We may now give another definition of entropy, which is more convenient than that in terms of the incurred waste, because it refers to the entropy of the working substance, without taking the whole isolated system into account, and because it is not given in terms of the lowest available temperature or the incurred waste. The new definition may be arrived at by considering reversible changes. If two bodies A and B are in contact, and are at the same temperature, and there is a reversible change so that the sum of the entropies of A and B remains constant, B can only increase its entropy by a corresponding decrease of the entropy of A. But the only way A can have its entropy reduced is by losing heat. For of the heat in A a part is available, and the rest, depending on the lowest available temperature, is waste. This waste can only be reduced by abstracting some of the heat of A. A

might lose work, but that would not reduce its entropy. We thus find that the entropy of a body can only be reduced by its losing heat. But it does not follow that if a body's heat is decreased it loses entropy. For if a gas is expanded in a cylinder so as to do external work without being supplied with heat from the outside, its heat is decreased. Its entropy is not, however, reduced, for, as already explained, the waste, once incurred, cannot be reduced; so that the entropy of a body cannot be reduced without at least an equivalent increase of the entropy of something else. The entropy of A can thus only be reduced by its losing heat to some other body. Merely diminishing its heat by converting it into work, or giving out the work, does not decrease its entropy. The heat must be given out so as to cause at least an equal simultaneous increase of entropy elsewhere. This practically means that for the entropy of A to decrease, heat must pass out across the boundary or envelope of A.*

* The only exception that comes to mind is the case where a thermo-circuit is arranged with a junction inside A. If the other junction is outside A, say in B, and B is colder, heat disappears from A and the entropy of A is reduced without heat passing across the boundary of A. But the other statement is still true: the heat is given out so as to cause at least an equal simultaneous increase of entropy elsewhere. There cannot be a single thermo-junction elevating heat into work with no corresponding degradation elsewhere in the circuit.

It may be similarly shown that the entropy of a body can only be increased reversibly by its taking in heat through its envelope. Consider an isolated system undergoing a reversible change, so that its total entropy remains constant while the entropy of one part A is reduced, and that of B increased by the same amount. A must give out heat, and if B increases its entropy without taking in that heat, that heat must go into some third body C, and increase its entropy to at least the extent that the entropy of A fell. There would then be an increase of the total entropy of the system, so that the change is not reversible. To make the change reversible B must increase in entropy only in proportion to the heat it takes through its envelope.* It must not be for a moment supposed that because the entropy of a body can only be increased reversibly by heat coming from outside through the envelope, it cannot be increased irreversibly otherwise. The entropy of a body cannot be decreased without giving out heat, either reversibly or irreversibly, and it cannot be increased reversibly

* The thermo-junction case is omitted from consideration here. B could in theory increase its entropy reversibly by means of a thermo-contact inside it; but even then, though its heat is not taken in as heat through its envelope, its increase of entropy, in a reversible change, is exactly balanced by the decrease of entropy of another body which does not lose the corresponding heat through its envelope as heat.

without taking in heat; but it can be increased irreversibly without taking in the corresponding heat through its envelope.

As the entropy of a body is decreased by giving out heat only, its entropy, compared with that of the same body in the standard state can be found by bringing it to the standard state by a reversible change or a series of reversible changes, and finding the heat given out and the temperature at which it is given out, and the corresponding entropy. If the heat H can all be given out at one temperature θ , then H/θ is the entropy, taking that of the standard state as zero. If the heat is given out at various temperatures, the entropy is $\int dH/\theta$. If the entropy of the body is less than in the standard state, as in the case of a block of ice at its melting-point, the entropy can be measured by finding the heat taken in during a reversible change to the standard state, and giving it the negative sign.

Definition.—We may therefore define the entropy of a body in state B, compared with its standard state A, as being numerically equal to the heat that would have to be taken in to get it from A to B by reversible changes, divided by the absolute temperature; or H/θ , if the heat is taken in (or given out if the entropy is less than in state A) at constant temperature θ , or $\int dH/\theta$ if the temperature varies. Thus the entropy of the body in state B is not a function of the heat actually taken in during its

change from A to B, as the change must have been partially, and may have been wholly, irreversible; but it can be measured as a function of the heat which would have to be taken in to change from A to B reversibly, or which would have to be given out if the substance were changed from B to A reversibly, which amounts to the same thing.

It is, perhaps, not unnecessary to point out again that though the entropy is measured in terms of heat that would have to be taken in, and the temperature at which it would come in in changing from A to B reversibly, the entropy is, in fact, always greater than H/θ or $\int dH/\theta$, as a reversible change never takes place. In a real change $\Phi > \int dH/\theta$; and while Φ is positive, $\int dH/\theta$ may even be negative—that is to say, the body may change from state A to state B, increasing its entropy all the time, and giving out heat all the time too. As every text-book on the steam- and gas-engine (except Rankine's*) defines entropy as $\int dH/\theta$ instead of as being measured by $\int dH/\theta$,

* Rankine is not clear about his “thermodynamic function.” His first definition makes it the same as entropy, but he also makes it equal to $\int dH/\theta$ without limiting the change to reversible change. He certainly did not develop the idea of entropy and its relation to waste, which forms the basis of this book. No doubt a man of his ability, if he had written on steam-engines somewhat later, would have been not only perfectly correct, but also clear and unambiguous in his statements and definitions.

if the change is imagined by a reversible path from A to B, this point cannot be insisted on too strongly. The incorrect definition makes the conception of entropy impossible to the reader ; and if the writer did not unconsciously depart from his own definition, it would make nonsense of thermodynamics.

As the entropy of a body can be measured by bringing it back to the standard state by reversible changes—that is to say, changes which involve no waste, and therefore no increase of entropy in the body and its surroundings—the entropy in state B, compared with state A, is measured by seeing how much entropy comes out on changing it from B to A without creating any entropy during the change.

The entropy of a body in a given state, therefore, depends only on the state, and not on its past history ; thus a quantity of steam in a given state as to pressure, temperature, and volume must give out the same entropy on being brought by reversible change to the state of ice-cold water, in whatever way it was made into steam.

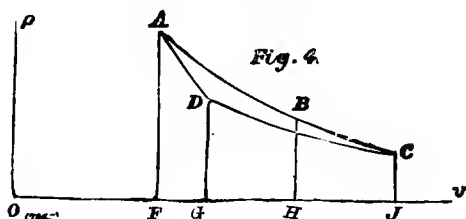
CHAPTER III.

THE $\theta\phi$ DIAGRAM.

WE may now deal with the $\theta\phi$ diagram, taking a simple case to start with, and discussing it from the point of view put forward in this article.

We may begin with the case of a perfect gas.

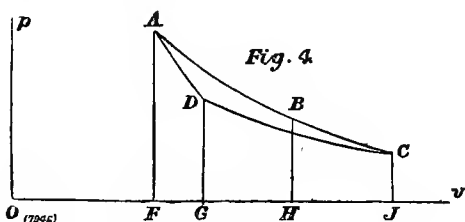
Suppose we start with a quantity, say, a pound, so that we deal with the specific volume and entropy



of a perfect gas in a cylinder with heat-tight sides, and let the area of the piston be unity, so that its pressure and volume are given by the point A in Fig. 4, where the height is the pressure on the piston, and the horizontal distance the volume of the gas. We may take the state A as standard for simplicity—that is, we take its entropy as zero. In the $\theta\phi$ diagram, to correspond with Fig. 4, we

therefore start with A to correspond with A in Fig. 4, marking off the height O A to correspond with the temperature θ_1 of the gas to start with, and on the line of zero entropy. Let the gas be now allowed to expand, doing external work w_1 and taking in heat h_1 , at temperature θ_1 the expansion being carried on reversibly to the volume and pressure represented by B, Fig. 4.

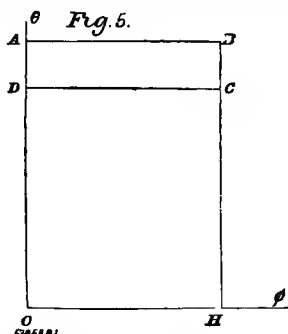
Consider the position at B. The gas has taken in heat h_1 , but it is no hotter; that is to say, some-



thing external, say a heat reservoir, has given out heat h_1 , which has crossed the boundary or envelope of the gas, and has then ceased to exist as heat, being converted into work w , which has gone outside, say, into a flywheel. But as the change is reversible, so that the entropy of the gas and the reservoir is constant, and as the reservoir has lost heat h_1 at temperature θ_1 , and the gas has taken in heat h_1 at temperature θ_1 , and has given out no heat elsewhere, its entropy must have increased by h_1/θ_1 . In Fig. 5, from A draw A B, so that A B

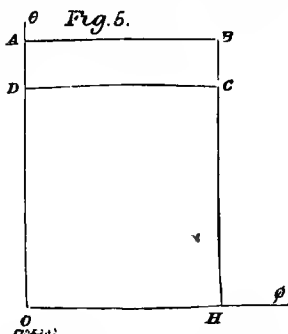
represents h/θ_1 , or ϕ . The height representing the temperature is constant, so A B is a horizontal straight line.

That the entropy of something outside, which supplied the heat h_1 reversibly, diminished, may seem an insufficient reason for saying the entropy of the gas is increased. But the gas cannot be compressed to its old state without giving out heat at some temperature, of which part must be waste.



The next step is to expand the gas from B to C reversibly, without taking any heat, but doing external work, so that the heat of the gas is drawn upon to do the external work. The entropy remains constant during the change, as the process is reversible. It could not reduce the entropy during this change, as no heat comes out across the envelope, and that is the only way the entropy could be reduced. As the change from B to C is reversible by hypothesis, the entropy of the gas cannot have

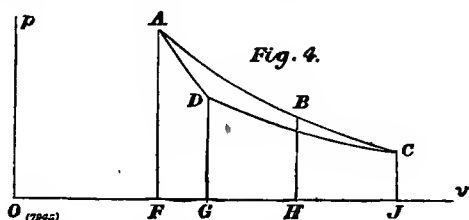
increased, else it would have to give out heat on reversal to get back to the state of B. From B to C then the temperature falls to, say, θ_2 , while the entropy remains constant. From B on Fig. 5 draw B C, so that the height of C represents θ_2 , the entropy D C being equal to A B. Let the gas be compressed isothermally and reversibly from C to D, giving out heat h_2 at temperature θ_2 until the



entropy is reduced to zero—that is to say, its original value.

On Fig. 5, the state point therefore moves along C D to D, where the temperature is θ_2 and the entropy zero, as at A. The gas is then compressed reversibly without any passage of heat across the boundary surface, until the gas reaches its old temperature θ_1 . If the temperature is θ_1 , the new state point must be on the curve A B, and as the entropy is zero, the new point must be A, which is the original starting point. We have thus gone

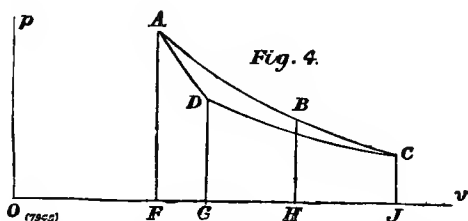
through the ordinary Carnot cycle, and Fig. 4 is the $p v$ diagram, and Fig. 5 the $\theta\phi$ diagram of it. As the cycle described is reversible, the curve A B, Fig. 4, is for a perfect gas, $p v = R \theta$, where, as the expansion is isothermal, θ is constant, and R is constant anyhow, so the curve is part of rectangular hyperbola, and is easily described with the help of a slide-rule. For instance, if $R \theta$ is found on one of the scales, and the slide turned round, and the 1 of the same scale put opposite



$R \theta$, the corresponding values of p and v are read off without moving the slide. As the height is equal to the pressure on the piston, and the length to the volume, the area A B H F is equal to w_1 , the external work done during expansion; and the area is also proportional to h_1 , the heat taken in at temperature θ_1 . In the $\theta\phi$ diagram, as the change from A to B is reversible, and at constant temperature θ_1 , the entropy, h_1/θ_1 , multiplied by θ_1 , is obviously equal to the heat h_1 , so the area A B H O (Fig. 5) is also, in this case, equal to the heat taken in

and to the work done. It is probably this that has misled people into supposing the $\theta\phi$ is a heat diagram, or that its area is proportional to some existing heat or to some work. Suppose the expansion from A to B had been carried out irreversibly without any heat being taken in by the gas, and without doing any external work. For instance, a partition might be put across the cylinder at A, to hold the gas, while the piston is moved to B. If a hole is now made in the partition, the gas will blow through into the vacuum, and eventually the gas will be, according to Joule's experiment, at the same temperature as before, and therefore at the same pressure, as the volume is the same. The gas has therefore got to state B without giving out any work, and without taking in any heat. It must be remembered that F A and H B represent the pressures on the piston, so that in the last case A B H F was equal to the external work w_1 . In this case there was no pressure on the piston during its movement. The passage from A to B was really not by the curve that joins them, but from A down to F, then to H, and up to B. There is apt to be some confusion as to what is meant by the pressure of the gas during such an irreversible change; but the only pressure that has to do with external work, which is the matter in question, on an indicator diagram, such as Fig. 4, is the pressure on the piston. We might have had an

indicator on the cylinder which would, if put on the gas side of the partition we inserted, have read pressure as $F A$ throughout the movement of the piston. In a steam- or gas-engine the indicator is merely to tell the piston pressure. An indicator put on this cylinder, unless put on the piston side of the division, would only give incorrect information. In a $p v$ diagram we are only concerned with the real piston pressure, not with any state of the gas.



If instead of using a partition, and opening a hole to let the gas through after the movement of the piston, we had used a very light piston and moved it suddenly so as to allow the gas to expand freely from A to B , immediately after the movement of the piston, we can imagine the piston moved so suddenly and quickly that during the movement there is no pressure on it, and therefore no external work is done. The gas then rushes into the vacant space, and the work of expansion of each of the little parts of the gas is spent on

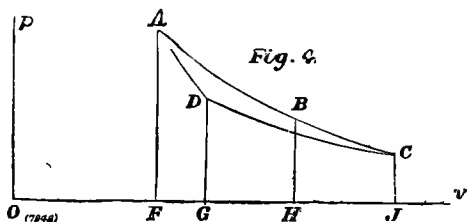
imparting kinetic energy to other parts of the gas. This is degraded again into heat, and the final result is that when the gas settles down to a uniform temperature and loses its kinetic energy, the pressure on the piston is $H B$, and the temperature θ_1 , and the entropy $A B$. It has been urged by men of science too, that in this case the increase of entropy is due to the production of this heat by friction in wiping out the kinetic energy; and in support of this contention it must be noted that if the gas puts all its work of expansion into kinetic energy, and that is then degraded into heat, the heat so produced will be equal to the heat h_1 that would have been taken in during the expansion if it had been reversible and isothermal. But the whole of the heat that is produced by friction in the reduction of kinetic energy in the irreversible expansion has previously disappeared from the gas in producing the kinetic energy. If the heat produced inside the gas by friction is to be counted as generated, the equal heat lost in producing the kinetic energy must also be counted, and the total internal generation of heat is then zero.

It has been urged that the increase of entropy in irreversible expansion is still due to the gas receiving heat, and the increase of entropy is still $\int dh/\theta$, even in an irreversible change. This is due to a misunderstanding of the meaning of the symbols. h is not the heat of the substance, nor the heat

gained by the substance. It is the heat taken in by the substance from the outside. It is the loss of heat suffered by some external reservoir or body. If you give h a different meaning, so as to include heat generated by any means inside the body without coming through the envelope or case as heat, h increases when a gas is compressed adiabatically—that is to say, without any heat passing through the envelope—and decreases during adiabatic expansion. And if the equation $\int dh/\theta = \phi$ were still true when dh meant the increase of heat of the body, the reversible adiabatic compression of a gas would not be isentropic. On the other hand, the isothermal reversible expansion of a perfect gas would be isentropic, because the heat taken in would be exactly balanced by the internal disappearance of heat which is converted into external work. It is important to remember that in these equations h , or H stands for the heat passed into the working substance, from outside through the envelope, and not for the heat of the substance, or for heat generated inside by friction, by internal combustion, by an electric resistance worked from outside, by compression or otherwise.

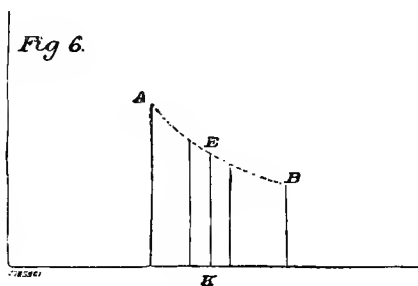
It may be asked what meaning the curve $A B$, Fig. 4, has when the expansion is quite irreversible—that is to say, all the increase of entropy of the substance is uncompensated by reduction of entropy elsewhere, and there is no external work. If the

piston is moved suddenly to B, after a little, the temperature, which varied throughout the volume of



the gas during the rush, comes to θ again, and the pressure to H B.

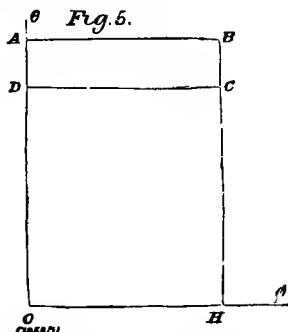
If the piston were first moved suddenly to a point, say, half way along, and stopped, the pressure would correspond to the vertical height, say K E, Fig. 6.



The piston might divide its whole stroke into a series of little quick steps, each being so quick that the gas exerts no pressure on the piston during its motion. The diagram will then be a sort of comb of vertical lines, the tops being in the curve A B,

and there will be no area and no outside work. If these steps are made more numerous and smaller, there will still be no area enclosed and no external work. The smaller each step is made, the smaller will be the variation of temperature throughout the mass during the little rushes of gas, and the variation of pressure as measured, say, against the sides of the cylinder.

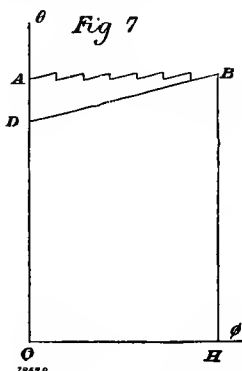
If the jumps are made indefinitely small, the



temperature of the gas remains uniform at θ_1 , and the pressure on the piston during its movement remains constantly zero, so that no actual work is done, and there is no area traced, yet the pressure of the gas on the walls of the cylinder follows the curve A B (Fig. 4) as if the expansion were reversible and isothermal.

Turning to the $\theta\phi$ diagram (Fig. 5), does similar reasoning apply? At B the temperature is θ_1 , and the entropy A B; but the question is, Does the

state point come along the straight line A B, or does it come round by O and H, so that no area is enclosed? or does it do something between the two? To come round by O and H would mean that the gas had no temperature, or was at absolute zero during the change, which is absurd. If the whole energy of expansion were first devoted to producing kinetic energy of the gas, equal to the external work



that might have been done by isothermal expansion, the temperature would fall to θ_2 ; and as the kinetic energy became degraded into heat, there would be an increase of temperature and entropy, so that the state point would move by a sloping curve from D to B. If the piston only makes small jumps, the state point will move much as in Fig. 7. The temperature will fall a little. It will be different throughout the mass of gas, but in no part will it

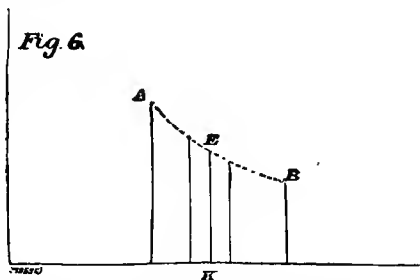
fall much. If the expansion takes place in a succession of jumps, the state point will make a succession of saw teeth; and if the jumps are indefinitely small, the state point moves along the line $A B$, tracing one side of the area $A B H O$.

We are justified, therefore, in drawing $A B$ straight as representing the movement of the state point in the $\theta \phi$ diagram; but this long explanation has been entered into rather to clear up difficulties than anything else. The area of the $\theta \phi$ diagram is not energy, but the area is important, for the excess of the area of the $\theta \phi$ diagram over the area of the $p v$ shows the badness of the engine from a thermodynamical point of view.

There is considerable confusion often as to the meaning of a $p v$ diagram; that is to say, as to what p means in an irreversible change. As a $p v$ or Watt diagram is to tell the work given out by the expansion, p is the pressure on the piston; so that the external work is $w = \int p dv$. In any reversible expansion the curve is also a diagram of the state of the gas; and people have been misled into supposing that the $p v$ diagram refers to the state of the gas in an irreversible change. This is the usual confusion about reversible and irreversible changes.

In Fig. 6 the dotted curve $A E B$ is the diagram of the equivalent state of the gas, and if p is taken as the height of this curve at any volume $\int p dv > w$, and the area does not represent external work.

Also $dh < p dv$. There are, in fact, two $p v$ diagrams—one in which p is the pressure on the piston, which is not a diagram of the state of the gas at all, and another which is unconsciously used instead of it, which gives the equivalent state of the gas, but not the external work. In reversible changes the diagrams coincide; in irreversible they do not, and we have two sets of pressures. Writers, for instance, often state that $dh/\theta = d\phi$, and that

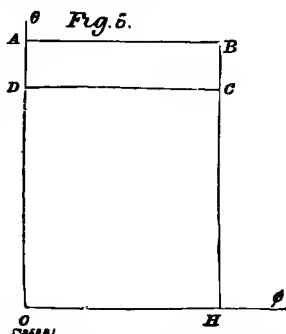


dh/θ and $d\phi$ are both complete differentials; dh/θ is not a complete differential in terms of the p and v of the diagram of the state of the gas in which $p v = R\theta$; $d\phi$, on the other hand, is a complete differential in terms of the ordinates of the state diagram in which $p v = R\theta$, but it is not a complete differential with reference to the external work or piston co-ordinates of the Watt diagram. $dh/\theta = d\phi$ would be true in the ideal case of reversibility when the two diagrams coincide.

As the change of entropy follows the state of the

gas, and not the external work, the $\theta \phi$ diagram is the same as before. At B the entropy is A B (Fig. 5), for at B the gas is in a given state, as to pressure, temperature, and volume, and, as already fully explained, the entropy depends on the state of the gas, not on how it got into that state.

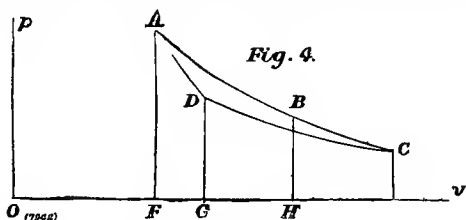
It is therefore incorrect to say that the area A B H O, Fig. 5, represents heat, for no heat was taken in. It is equally incorrect to say it represents



external work, for no external work was done. Thus entropy is not a factor of heat; it is not heat-weight, and it is not a factor of energy. It is not h_1/θ_1 , for no heat has been taken in, and the temperature has been constant. Neither is it equal to $\int dh_1/\theta$. It is, to repeat, a quantity which, when multiplied by the lowest temperature available, gives the incurred waste. Thus, if, for example, θ_2 is taken as the lowest available temperature, the gas may be expanded reversibly without change of

entropy from B to C, and may then be compressed isothermally along C D, Figs. 4 and 5, giving out the heat h_2 at temperature θ_2 . This is represented by the area D C J G, Fig. 4, and D C H O, Fig. 5. The area D C H O is thus the waste that must at least result from bringing the substance from a state where its entropy is A B or C D back to the standard or zero state.

The waste has not yet taken place when the gas has got to B, even irreversibly; but to get it to A

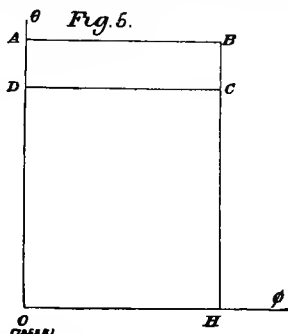


again, work must be degraded into heat, of which O D, the lowest available temperature, multiplied by the entropy A B, gives the waste D C H O. That is why the expression "incurred waste" has been used. The waste does not take place necessarily when the entropy increases; but as it must take place eventually, it is called "incurred." There is still another reason for the expression. In reality reversibility is unattainable, so in bringing the gas back from B to A a little more waste must result. But this waste is not "incurred" when the gas is at B; it is a subsequent product, due to the

difficulty of approaching reversibility in the changes necessary to bring the gas back to A.

The other definitions given also fit the case.

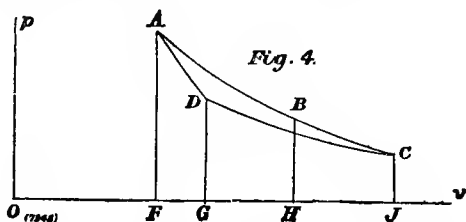
The entropy of the gas at B is numerically equal to the heat that must be given out on returning to A by reversible changes, divided by the temperature of the surface at which the heat is given out.* Thus, if the gas is brought back isothermally along B A, Fig. 4, the heat given out at temperature θ_1 is



proportional to the area A B H O, Fig. 5, and that divided by O A is A B. The same reasoning applies to the path B C D A, Fig. 4, where the heat H_2 or D C H O, Fig. 5, is given out.

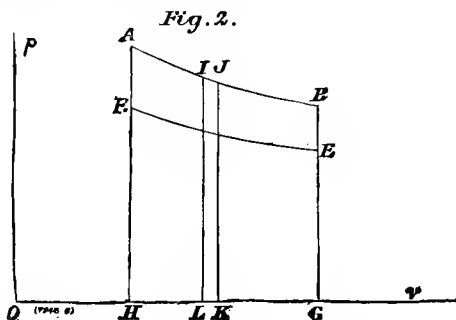
* In this sense entropy might be called a factor of heat, but that is not at all the sense in which it is so termed. If a body has entropy Φ to get it the standard state where $\Phi=0$, heat H , so that $H/\theta=\Phi$ or $\int dH/\theta=\Phi$ must at least be given out, but that heat may have to come from external work, and the entropy of the body is not a factor of some heat of unknown amount that is going to be produced at a future date from some external energy or other.

The curve B C, Fig. 4, may be easily drawn with the help of a slide-rule and proportional compasses. Its equation is $p v^\gamma = \text{constant}$. This is shown in the text-books, so it need not be gone over again, as



the object of this book is rather to be supplementary and explanatory, and not a complete self-contained treatise on elementary thermodynamics.

As we know the value of $p v$ at B, we can find the



value of $p v^\gamma$ there, if we know γ . For a perfect gas, γ is 1.6; we therefore find $p v^\gamma$. Starting from B, Fig. 2, for instance, we multiply the corresponding p by the corresponding v^γ , and note the

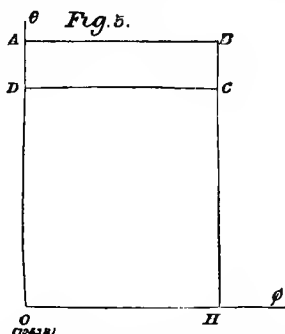
number on the slide-rule scale. The proportional compass is set at 1.6. For every pressure the remainder of the scale up to $p v \gamma$ is spanned by the long legs of the compass; the short legs then give the corresponding v on the same scale.

The word "adiabatic" means without passing through, denoting that during an adiabatic change there is no crossing of heat into or out of the gas. The heat of the gas may vary, of course, but by changing to or from work. If it were reversible, an adiabatic would be an isentropic change. But the entropy can increase without any heat coming in, and, in fact, always does; so an adiabatic change never is, in fact, isentropic.

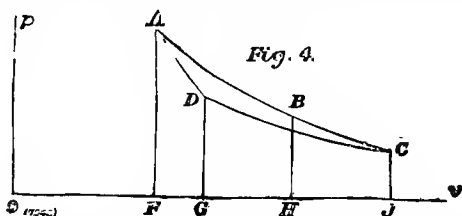
Text-books frequently treat isentropic and adiabatic as synonymous terms—a very widespread error, arising, like the others, from ignoring real as opposed to hypothetical thermodynamics.

It will be noticed, on comparing the $\theta \phi$ and the $p v$ diagram for the Carnot cycle of Figs. 4 and 5, that if the diagrams are drawn to suitable scale, while the work point in the $p v$ diagram traces the first step from A to B, the state point on the $\theta \phi$ traces A B. The area A B H F on Fig. 4 is then equal to the heat h_1 taken in at θ , and to the external work done from A to B. The heat of the perfect gas remains constant. The corresponding area, A B H O, Fig. 5 is also equal to the heat h_1 taken in at temperature θ_1 . But the area A B H O does

not represent the increase of heat of the gas. The diagram is not a heat diagram, in fact. From B to C the area B C J H represents the work done by the gas, but there is no heat taken in or given out; but



the gas loses heat, which goes out as work. The state point in the $\theta \phi$ diagram merely descends. The other two steps are similar, but in the opposite direction. The result is that the area A B C D is



equal on these diagrams. The efficiency in Fig. 4 is the ratio of the area A B C D to the area A B H F. The efficiency in Fig. 5 is the ratio of the area A B C D to A B F O, and is much easier to see,

and is obviously proportional to $(\theta_1 - \theta_2)/\theta_1$. But that is only true of the reversible cycle; if the cycle is irreversible, for instance, on account of the expansion from A to B being free, Fig. 5 does not give the efficiency. It is worthy of remark that in the reversible cycle the entropy alters during the changes in which the heat of the gas remains constant, while the entropy remains constant during steps two and five, in which the heat varies.

$\theta \phi$ Diagram for Steam.—Instead of taking a perfect gas, steam may be taken. Water at the temperature of ice is generally taken as standard of comparison. The water-steam diagram may therefore be started from 32° Fahr., or 493° F.A., or Fahrenheit absolute. The unit of heat used by English engineers is the heat necessary to raise 1 lb. of water 1° Fahr., namely, from 59° to 60° . It is a pity there is a special unit of heat. It is a survival of the times when people did not fully realise that heat is energy; but there is no reason why we should still have a separate unit of heat. But as we have the foot-pound and, I think, the poundal,* as units of energy, perhaps a special unit of heat saves confusion. The heat necessary to raise 1 lb. of water 1° Fahr. is called the British

* I think poundals are energy, but they may be force, or a kind of yellow cakes. I do not remember, and am not anxious to know.

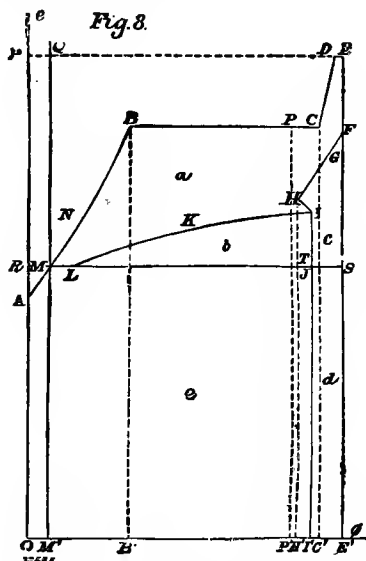
thermal unit; and a quantity of heat is measured in British thermal units.*

The Institution of Civil Engineers has recently recommended officially that "British thermal unit" be shortened into B.Th.U. as opposed to B.T.U., which stands for "Board of Trade Unit," an irregular and barbarous name of 3,600 joules. No doubt British thermodynamicians are getting so efficient in manipulating their units that inaccuracies due to the interchangeable use of the British thermal and the Board of Trade unit are becoming perceptible. The letters B.Th.U. will, therefore, be used to denote these things.

To raise water 1° at a given temperature, or sensibly at that temperature, needs 1 B.Th.U. per lb., so the increase of entropy per degree is $\frac{1}{\theta}$ or $\frac{d\phi}{d\theta} = \frac{1}{\theta}$; provided the specific thermal capacity, inaccurately called the "specific heat," of the water remains constant. The $\theta\phi$ curve for water is

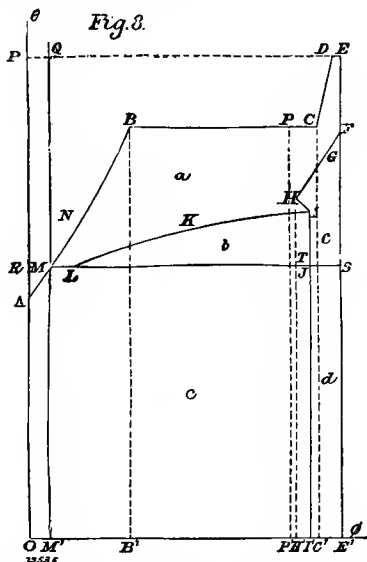
* Lord Kelvin and others have pointed out that this use of the word "units" is incorrect. The guinea, pennyweight, perch, quartern, bushel, acre, kilderkin, hand, baker's dozen, ream, em, month of Sundays, and blue moon are British units, so that a statement as to, say, 31,416 British units would refer to a sort of museum that could easily be collected. But it is no use being too pedantic over such things. What is wanted is a name for the British thermal unit, such as the therm, then we could say that the water took in so many therms. It would be simpler still to say so many foot-pounds.

thus such that the rate of increase of the horizontal line is inversely as the height. As $\frac{d\phi}{d\theta} = 1/\theta$, $\phi = \int \frac{1}{\theta} d\theta = \log_e \theta + \text{const.}$ The $\theta \phi$ for a substance whose thermal capacity remains



constant is thus a logarithmic curve, and the constant is chosen so that the curve cuts the ordinate O P, Fig. 8, at the height corresponding to 493° Fahr. This curve can be easily plotted by calculation, and more easily copied from a steam table or Sankey's valuable steam chart. The steam chart, for which engineers are deeply indebted to Captain

Sankey, shows properties of steam graphically, being a $\theta\phi$ diagram with curves giving every possible information carefully plotted on it. The statement that a square of a given size is a British thermal unit need not be regarded.*



It need hardly be mentioned that it is much easier to work all thermodynamical calculations on the metric and especially the C. G. S. system; but there seem to be no convenient tables available.

* For accurate work a correct steam table or chart is necessary. Probably the National Physical Laboratory will soon check Regnault's experimental figures. The present steam tables are in urgent need of careful revision.

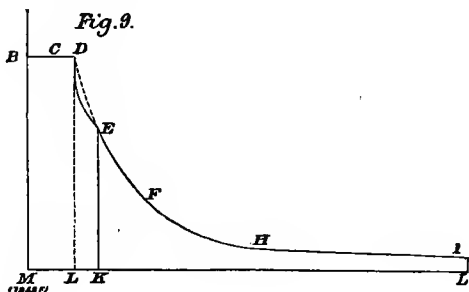
It is one of the strongest arguments against the adoption of the metric system in this country that Continental people, even scientific people, who could use it without any difficulty, generally try to avoid its use. A steam table, with the temperatures in degrees from freezing-point, the pressures in millimetres of mercury, atmospheres, or kilogrammes, instead of megadynes per square centimetre, the heats in calories instead of joules, and the entropies not given at all, is not convenient; and it is easier, even if it is desired to work on the metric system, to use the English—or rather American—steam tables, such as Peabody's or Reeve's. Peabody's and Reeve's can both be got separately,* and Reeve's are especially complete and convenient. The expression "Entropy of the Heat-Energy" at the head of the table does not make the data inaccurate.

Starting from 492.8° F.A., Fig. 8, the curve during the heating of the water is practically logarithmic. It would be accurately logarithmic if the specific thermal capacity, or specific "heat" of the water were constant. The curve is easily got from the temperature T , and entropy N , columns,†

* Messrs. Wiley & Co. and Messrs. Macmillan & Co.

† It seems a pity to introduce a new letter, N , for entropy, Rankine used ϕ for the thermodynamic function, and Clausius used S for entropy. Maxwell used θ and ϕ for temperature and entropy. Gibbs used η for entropy. T and t are con-

and as the curvature is very small, a few points are enough. Suppose the water is heated up to 850° F.A., omitting decimals, before steam begins to form. The table gives 220 lb. per square inch as the pressure, and the volume is inappreciable. The indicator or $p v$ diagram may be drawn at the same time (Fig. 9) with the lettering to correspond. The $\theta \phi$ diagram, so far, is a piece of a logarithmic curve, and at 850° F.A. the entropy is 0.552. This



means that, to get the water back to the standard temperature of 493° F.A., $493 \times .552 = 272$ British

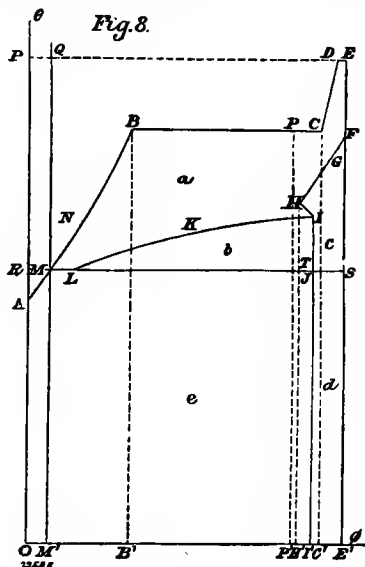
venient for absolute and thermometer temperatures, but T is already in use for kinetic energy, and this gives rise to confusion in dealing with thermodynamics and the kinetic theory of gases together. The Germans often use s for temperature. Quantity of heat taken in by a body is generally written Q , but as Q in other branches of physics denotes the quantity factor of energy, and not energy itself, H is more accurate. θ , ϕ , and H are therefore used here, following Maxwell and others, though T , S , and Q are more general, especially in scientific books and papers.

thermal units must be wasted, if 493° F.A. is the lowest available temperature. It does not follow that this waste has been caused by warming this water. If the 0.552 was compensated entropy—that is to say, if the increase of entropy of the water was exactly balanced by an equal decrease of entropy of whatever supplied the heat—there was no increase of total entropy, and therefore no new waste incurred. If, on the other hand, the water was sensibly at the same temperature throughout its volume at each instant, but was heated by gases at a much higher temperature, there was a growth of uncompensated entropy outside the water during the heating. The growth of entropy due to heat conduction will be discussed presently. In the case of heating water, practically all the energy taken in, whether as heat, or as work which is degraded into heat in the body of the liquid, is in the form of sensible heat, and it might appear that the entropy was a factor of the heat; for though $\int dh/\theta < \phi$, where h is the heat taken in as heat, if the process is not reversible, $\int du/\theta = \phi$ is very nearly true where du is the differential of the sensible heat of the body. It is not quite true, however. The water can do external work during the expansion, and then even $\int du/\theta < \phi$. It is quite clear that the entropy of the water at B—that is to say, at 850° F.A. is 0.522, however the heating has been carried out. Text-books on the steam-engine define the

entropy as $\int dh/\theta$, but if the water is heated in any other way than by taking in heat from the outside—for instance, by heating by Foucault currents produced in the water by a rapidly changing electrical field— $\int dh/\theta$ might be zero if the water took in no heat, and negative if it gave out some as it heated. It cannot be too often urged that the entropy of a body depends on its condition and not on its history. Unless all the changes are reversible, $\int dh/\theta$ depends on the history, not on the condition of the substance. If the writers of the text-books stuck to their definition of entropy when working with irreversible processes, they would come to grief at once; but they unconsciously avoid the abyss that ought to yawn for them by taking their data from steam tables or Sankey's chart, which is correct, because the entropy then depends on the state of the substance and not on $\int dh/\theta$.

Continuing the diagrams, suppose all the water vaporised at pressure 220 lb. and temperature 850° F.A. The $p v$ diagram is traced by the constant pressure line B C to 2.1 cubic feet. The state point on the $\theta \phi$ diagram goes to $\phi = 1.537$. At the point C the $p v$ diagram shows the external work done by the steam in expanding. It does not matter whether the steam is in the boiler or the cylinder for the moment; the work is done outside the steam during expansion. We may assume the steam to be in a hypothetical cylinder. Part of the

heat taken in is converted into work—namely, 84.8 British thermal units, and this is shown on the $p v$ diagram. 753 British thermal units have been devoted to vaporising the water. This energy is still in the steam. The allocation of the energy



taken in by the water in evaporating, which we will assume was taken in as heat, might be shown on $\theta \phi$ curve. The area $A B B^1 O$ then represents the sensible heat which raised the temperature of the water, or it so nearly represents the area that it may be taken to represent it. The variations of specific thermal capacity of water are small. The vertical

ordinate is temperature, the horizontal entropy. Take now the area $B C C^1 B^1$; it does not represent the increase of heat of the water from B to C , so it is not a heat diagram; neither does it represent the increase of energy of the water from B to C , so it is not an energy diagram of the steam. It is a $\theta\phi$ diagram, and the length $B C$, multiplied by the lowest available temperature, gives the waste. Also the area $B C C^1 B^1$ gives the heat that must at least be given out at temperature $B_1 B$, or 850° F.A., to get the steam back into water at the same temperature; but this heat would not all be provided by the steam; some of it must come from outside, generally as mechanical work. As frequently explained, entropy is not a factor of heat. Suppose we adopt a suitable factor χ , so that $\theta\chi$ is the increase of energy in the form of heat in the body itself if the temperature has been constant, and $\int \theta d\chi$ is the increase of heat from the standard state when the temperature varies. It must be pointed out that splitting heat into factors θ and χ , so that $\int \theta d\chi$ is energy, is unorthodox. There has for a long time been a sort of hazy idea in thermodynamics that heat should be split up into a tension and a quantity factor, like other forms of energy. Taking temperature as one factor, capacity for heat has been proposed as the other; but that is obviously absurd, as, if C is the capacity, the energy would be $\int C d\theta$, not $\int \theta dC$. Besides C is capacity for

energy not for a quantity factor, so that capacity for heat is by no means the analogue of capacity—in, say, hydraulics or electricity. As has been frequently mentioned already, the error that entropy is a factor of energy, is very widespread, not only among physicists and engineers, but even among many who write specially on thermodynamics. I brought a paper before the Physical Society about two years ago, in which it was pointed out that, although in a reversible change ϕ is numerically equal to the factor of energy—lost as heat by the external reservoir, not gained as energy by the working substance—corresponding with temperature, $\int \theta d\phi$ is not energy in a real change. The paper discussed the question of splitting heat into factors of energy, and compared the advantages and drawbacks. The paper was rejected, however, and until scientific men generally attend to real partly irreversible processes, the subject cannot come forward for discussion. It is fair to point out as far as possible where my treatment is not orthodox, so that the reader does not willingly absorb without criticism, as established thermodynamics, what are really the heterodox ideas of the writer.

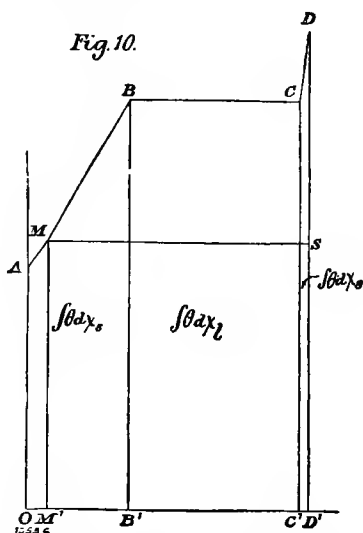
As we have to deal with sensible heat, the heat that makes things hot, and latent heat, which changes their physical state, for instance, the difference of internal energy between steam and water at the same temperature, we may use suffixes, so

that χ_s is the quantity factor of sensible heat, and χ_p that of latent heat of physical change.* We may now plot the heat energy of the pound of water from A to C. From A to B we get the figure A B B¹ O, Fig. 10, in which the height is θ and the breadth χ_s , so that the area is $\int \theta d\chi_s$, giving the sensible heat of the water at 850° F.A., neglecting any question of variation of specific capacity. From water to steam at $\theta = 850^\circ$ the water takes in 837.7 British thermal units of energy, of which 753 remain as latent heat, and 84.7 go out as work.

* The expression "latent heat" is used absurdly in thermodynamics. Thus, if ice is melted, heat is taken in and remains in the water. The alteration of volume is minute. If, on the other hand, water is evaporated into steam doing external work, the external work is included in the so-called "latent heat." There is the same confusion as regards the mis-called "specific heat." The heat absorbed per unit mass at constant volume may be measured by a specific thermal capacity at constant volume; but to measure the heat absorbed at constant pressure or temperature by a "specific heat at constant pressure" or a "specific heat at constant temperature" is absurd. In the case of a perfect gas, for instance, the difference between K_p and K_v is entirely external work, and not heat at all; and the "specific heat at constant temperature" is entirely external work. The whole nomenclature of thermodynamics demands re-modelling.

By latent heat in connection with χ_p is meant that $\int \theta d\chi_p$, or generally $\theta \chi_p$, is the heat taken in and kept by the substance itself during a physical change such as fusion or evaporation; and it does not include any external work. Similarly $\int \theta d\chi_c$ is the heat of chemical change. We are not concerned with that at present.

As θ is here constant, $\chi_p = 0.9$, and we may add a rectangle $B C C^1 B^1$, to represent $\theta \chi_p$, to Fig. 10. As this rectangle is the same height as the larger rectangle in the $\theta \phi$ diagram, we might cut an equal area off that area $B P P^1 B^1$. This area would



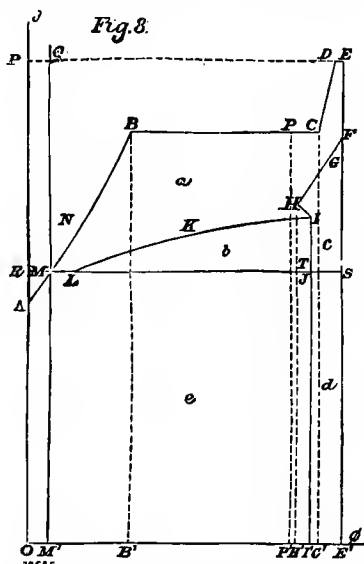
represent the increase of latent heat of the water from B to C , and the remaining area $P C C^1 P^1$ would represent the external work. This division of the $\theta \phi$ area into two areas representing $\theta \chi_p$ and w is not really legitimate. The quantities have no real place on a $\theta \phi$ diagram; and it is only because the temperature is constant that they can be superposed that way. The diagram would look

as if the latent heat had been completed first, and as if there were a state P in which all the water was evaporated, and no external work yet done. More than this, there might have been no work corresponding to the small area $P C C^1 P^1$. For instance, the water might have been evaporated at a pressure of 220 lb. and blown through a small hole into a space big enough to hold all the steam at the same pressure and temperature. This process would be irreversible, and the area $P C C^1 P^1$ would represent external work that might have been done, but was not. The entropy would be the same in both cases, so would χ_p . The work that might have been done, but was not, has been called "uncompensated work," I think, first by Duhem, to correspond with the idea of uncompensated entropy. The term is not happy, because the work does not exist. Uncompensated entropy is a quantity that is produced, without the redeeming compensation of reduction of entropy elsewhere. Uncompensated work is not produced at all. Entropy is a kind of drawback, so uncompensated entropy is an unmitigated drawback. But work is the other way. If a British workman unit is paid for work he does not do, it would not express the employer's feelings to say the workman did uncompensated work. It is the wage that is uncompensated. It is on such grounds that I venture to differ from so eminent an authority as Duhem. The uncompensated work is

thus the difference between $\int \theta d\phi$ and h . "Uncompensated" work is thus work that might have been gained, but was not. "Ungained work" might be a better term for it. It is the product of the uncompensated entropy and the temperature if that is constant, or $\int \theta d\phi_u$ when it is not, ϕ_u being the uncompensated entropy. The ungained work at any temperature θ_1 is to the corresponding incurred waste as θ_1/θ_2 , where θ_2 is the lowest available temperature. Where a reversible change takes place there is no uncompensated entropy and no ungained work. The change is then said to be made at constant "thermodynamic potential"—another rather unfortunate term. The reversibility of a change can be expressed wholly in terms of the co-ordinates of the substance, such as the pressure, temperature, volume, entropy, latent heat, chemical energy, &c., without reference to the outside conditions. These expressions were worked out by Helmholtz, Massieu, and Gibbs, and are now generally known as Gibbs's functions or thermodynamic potentials. If these functions were expressed clearly in words, instead of being treated as obscure results of pages of differential equations, they would be quite useful to engineers. If the common statement that the area of the $\theta \phi$ is the same as, or proportional to that of the $p v$ diagram were correct, there would be no such thing as ungained work, and there would be no such thing

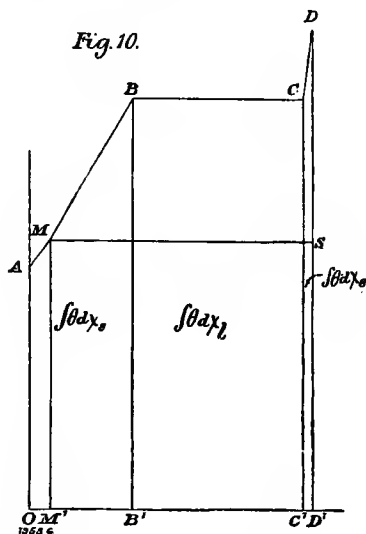
as waste, and all steam and gas-engines would have an efficiency of $(\theta_1 - \theta_2)/\theta_1$, and there would be no need to study their thermodynamics, as they would be incapable of improvement.

Let the steam now be superheated to, say,



1,000° F.A. at the same pressure, and reversibly. The $p v$ diagram shows a corresponding increase of volume, and the state point rises to D. A new area under C D is thus added to the $\theta \phi$ diagram. The added heat is thus partly converted into external work, and partly converted into sensible heat, making the steam hotter. We may add a curve

C D to the $\theta \chi$ diagram, Fig. 10, so that the height is θ and the breadth χ_s and the area $\int \theta d\chi_s$ is the increase of sensible heat during the superheating. The area under C D, Fig. 10, is less than that under C D in the $\theta \phi$ diagram, Fig. 8, because the breadth of the heat diagram is χ , the factor of heat,



and of the $\theta \phi$, ϕ the entropy, which is always, in fact, greater. The difference in area between the heat diagram and the $\theta \phi$ diagram is thus the external work if the change has been reversible, and the external and “uncompensated” or “ungained” work if it has been wholly or partly irreversible. What was said about its not being legitimate to

divide the area $B C C^1 B^1$ of the $\theta \phi$ diagram into two areas $B P P^1 B^1$ and $P C C^1 P^1$, one representing heat and the other work, is now clearer. The $\theta \phi$ area under $C D$, Fig. 8, with its curved top, cannot be divided into a heat area $C D D^1 C^1$ of the heat diagram, and an external work area by any vertical line. In fact, the heat diagram, Fig. 10, is itself unlawful, for it has two separate kinds of heat on the same area. Thus, if the steam did not behave as a perfect gas during heating, but stored up some latent heat, the area $C D D^1 C^1$ on the heat diagram would really represent $\int \theta d\chi_s + \int \theta d\chi_p$, and the area could not be divided out into latent and sensible heat. The area of the heat diagram (Fig. 10) above the lowest available temperature, $M S$, is the available energy of the steam in relation to the state point M . That energy can be got as work by going round from D to M by S reversibly.

From D suppose the steam to be expanded isothermally, but partly reversibly and partly irreversibly. If the expansion were wholly irreversible, no heat would be taken in and no work done, and the trace of the $p v$ diagram would be $D L K E$; whereas if the change were reversible, the trace would be by the bit of hyperbola $D E$ shown dotted. If it is partly reversible, the pressure will be less than for the hyperbola, and it may be as in the full curve $D E$. The area on the $\theta \phi$ diagram under $D E$ is the same whether the path in the $p v$ is by

the dotted or full line, and is equal to the area D E K L of the $p v$ diagram, taking the dotted line, and the difference is the "ungained" work. No part of the area under D E of the $\theta \phi$ diagram is thus heat, assuming the superheated steam to be a perfect gas. In reality, allowing for steam not being a perfect gas, the increase of entropy D E should be a little more, and the small difference should cover an area $\theta \chi p$ which should be added to the heat diagram. That may be neglected.

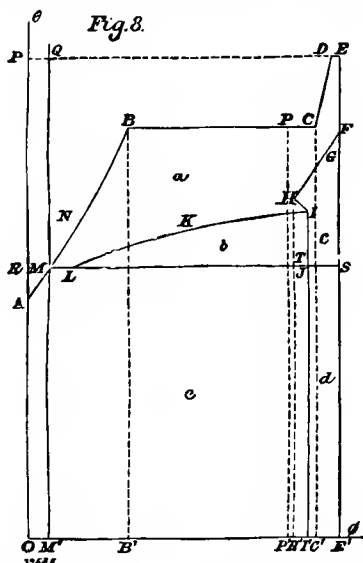
The superheated steam may now be expanded in a heat-tight non-conducting cylinder, in a cylinder which gives up heat to the steam as it expands, or in a cylinder that abstracts heat. In order to make the discussion as complete as possible we may take some of each. Then the steam may expand reversibly doing the full complement of external work, or wholly irreversibly doing no external work, or partly irreversibly doing some external work. The reversible and irreversible expansion of a perfect gas have already been discussed.

If the steam now expanded without doing any external work, its state point would move to the right of E on the $\theta \phi$ diagram, and the $p v$ diagram would go down E K, and then the volume would increase at zero pressure. If the cylinder gave up enough heat to keep the steam at the constant temperature of 1,000° F.A., and the expansion was

and therefore isentropic. From F the steam will be supposed to be expanded in another cylinder, which abstracts heat during the expansion; so that the $p v$ curve F H bends down below the reversible adiabatic line; and the state point on the $\theta \phi$ diagram moves from F to H, showing fall of temperature and decrease of entropy going on together. This curve F H will cut the saturation line at G, so that at H about 0.2 of the steam has been condensed. From H to I let the expansion be neither adiabatic nor isothermal, so that the cylinder walls give up heat to the steam, and the entropy thus increases, and the temperature falls. At I let the exhaust open to a condenser at lower temperature than the steam, say, as represented by the height of the line M J. When the steam has all fallen to this temperature, the entropy will be reduced, and the state point will be at the point L. How it gets from I to L will be discussed presently. At L we have nearly a pound of water and a little steam occupying a large volume. As the piston comes back the steam is all condensed to water, and we get, not to A, the freezing-point, but to M, which is not at zero entropy.

It need hardly be said that the $p v$ and $\theta \phi$ diagrams here discussed are not practical at all; they are merely put together on paper to illustrate the theory of entropy. In practice the indicator diagram and the steam per half stroke is the starting point,

and there is only a very rough approximation to knowledge of what happens. In the present examples the $\theta \phi$ diagram is made up from steam data and an imaginary $p v$ diagram, as if of a single cylinder with no clearance or cushioning, and many pecu-



liarities not met with in practice. A $\theta \phi$ diagram with straight lines and corners, and a right-hand side like Fig. 8, is not found in steam work.

The $\theta \chi$ diagrams need not be discussed further, as it is beyond the scope of this book to discuss factors of heat; they were introduced here to show the difference between the $\theta \phi$ and real heat diagrams.

In order to keep the diagram clear, vertical lines are drawn dotted from the various state points to the base, and the corresponding letters with accents are put on the base line for reference. As it is tedious to follow a diagram with polygonal areas denoted by numerous corner letters, areas are marked with small letters, each letter denoting the area enclosed by hard lines. Thus $a + b$ is the area M B C D E F H I J L M.

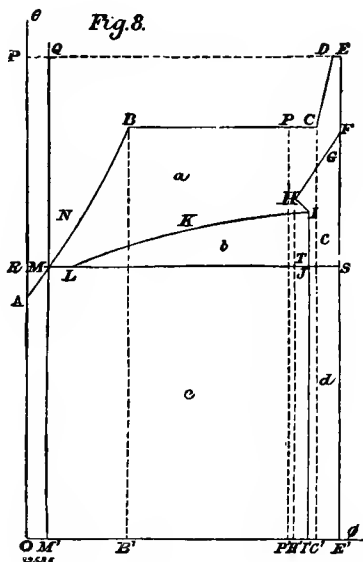
At E the entropy is at the maximum value touched during the cycle. To find the incurred waste at E the increase of entropy is multiplied by the lowest available temperature. For simplicity the same pound of water may be supposed to be used over and over again. So the waste is not the distance P E multiplied by the lowest available temperature, as the entropy never falls below R M, corresponding to water at the temperature of the condenser.

Making P Q = R M, Q E is the maximum increase of entropy during the cycle. Choosing 32° Fahr., or 493° F.A. as zero of entropy, is purely arbitrary; in this case water at temperature O R might have been taken as the standard—that is, as having zero entropy. Taking Q E as the increase of entropy at E, the next question is, What is the lowest available temperature? The lowest temperature reached is at L M, so the waste incurred up to the point E is the area $e + d$; but the waste is really considerably

tropic adiabatic change. If the change is reversible and isentropic, it is also adiabatic, and the path is vertical; but suppose the steam were wire-drawn between E and F, its entropy from that cause would increase; but if, at the same time, it lost heat to the valve or other metal-work so that its entropy was reduced by loss of heat exactly enough to counterbalance the increase by irreversible expansion, the trace would be vertical. These doubly irreversible disturbing causes would have additive effects in reducing the area of the $p v$ diagram relatively to the $\theta\phi$.

Matters are complicated in Fig. 8 by the leftward slope F H, and the next slope H I. It need hardly be repeated that such a corner as that at H does not occur; it is shown simply as an example. At E the incurred waste was $d + e$. From F to H the entropy is reduced, and at H the incurred waste is $M T H^1 M^1$. It might therefore be supposed that from F to H the actual waste is the difference in entropy of F and H multiplied by $M^1 M$. But $M^1 M$ is not the lowest available temperature here at all. The entropy from F to H has been reduced by giving up heat at a varying higher temperature, not to a condenser, or to anything where it can be utilised, but to cylinder walls, where it may be conducted away and wasted absolutely. The waste corresponding to the change F H is thus the area $H F E^1 H^1$. If the heat given

to the cylinder walls were used in a little engine, some of this would be recovered, and the waste would be less. The waste may also be reduced by some of the heat being given back to the steam later on.



From H to I the steam is receiving heat from the cylinder walls. If this heat is supplied from the furnace, for instance, by a jacket, the incurred waste at I exceeds that at H by the area $T J I^1 H^1$; we thus have a vertical strip of waste area $T J I^1 H^1$ which has to be reckoned twice. If the heat supplied between H and I was some of that

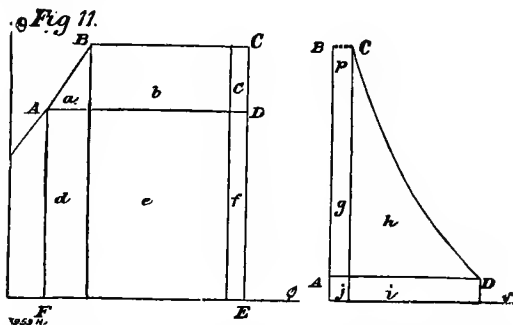
parted with between F and H to the cylinder walls, the waste due to F H, which was taken as $H F E^1 H^1$, has been over-estimated, and instead of the narrow strip $T J I^1 H^1$ being reckoned twice, it must be reckoned once only. The result is that the waste from F to H—that is, the heat now useless—is the area $c + d$, so that the strip under H I is only counted once, and the little area H I J T would be saved, or utilised if the lower line M J of the closed cycle were the lowest available temperature. If the curve I K L is the lowest available temperature, the area H I J T is reduced to a little triangular piece at the top.

The next point is the passage from I to L. The difficulty is that while the steam is blowing through the exhaust, the part that is condensed is at condenser temperature, while the part that is in the cylinder begins by being at a higher temperature, and the temperature gradually falls. There is no one value for the temperature during the change. The best thing to do, therefore, is to make some assumption which will cause no error in deriving results from the $\theta\phi$ and $p v$ diagrams, and will at the same time give a meaning to θ during this change. One method is to assume that the steam, instead of rushing off to a condenser, is cooled to condenser temperature at constant volume. This gives the curve I K L (Fig. 8). Another assumption might be that the steam expands adiabatically

diagram is wrong. It is always greater, and the difference is the ungained work and the "lost work," which has not yet been discussed. Cutting off a corner like I K L, therefore, looks like reducing the area of the $\theta \phi$ cycle, so as to lessen the difference of area, and therefore lessen the ungained work. It might therefore appear that the $\theta \phi$ diagram showed that exhausting above condenser temperature is rather a good thing than otherwise, and therefore the $\theta \phi$ diagram is misleading. This would be, however, an incorrect view. The ungained work is not lessened by raising the lower side of the $\theta \phi$ cycle. Thus, if there was some ungained work during the increase of entropy from B to C, it might be regarded as represented by an area of height B B or C C, and width equal to the uncompensated entropy. It stretches right down to the bottom of the diagram. This is an area by which the $\theta \phi$ cycle exceeds the $p v$ cycle, therefore, whatever the height of the lower line of the $\theta \phi$ cycle. If the lower side of the $\theta \phi$ cycle were raised until it coincided with the upper, and the ungained work were as before, the area of the $p v$ cycle would be negative, and numerically equal to the ungained work; that is to say, the steam would expand doing no external work, and the engine would do work equal to the ungained work in compressing it into water again.

The theory of ungained work may be shown

better by a simple diagram. Suppose water at A in the $\theta \phi$ and $p v$ diagrams, Fig. 11, were heated reversibly to B, then expanded to C reversibly and isothermally, and then expanded to D reversibly and adiabatically, and finally compressed to A again, also reversibly. Assume the $p v$ diagram, Fig. 11, to be drawn to correspond in scale with the $\theta \phi$, and let the areas be cut up by the vertical and horizontal lines into small areas which do not overlap, each with its letter of reference. Taking



the four steps, and putting down the intake of heat and output of work, we have :—

Step.	Heat Taken in.	Work Done.
A to B	$a + d$	0
B „ C	$b + e + c + f$	$c + f = g + j$
C „ D	0	$a + b = h + i$
D „ A	$-(f + e + d)$	$-f = -(i + j)$
Balance	$a + b + c$	$a + b + c = g + h$

If, however, the expansion were wholly irreversible, to take an extreme case for simplicity, the statement would be:—

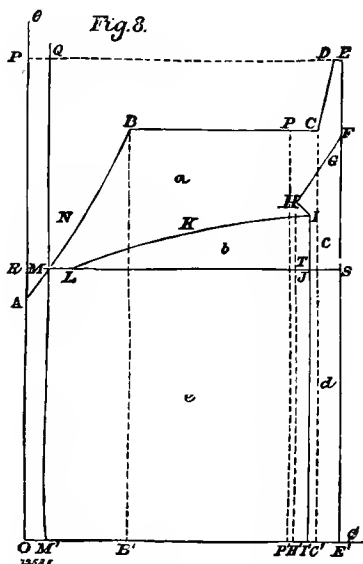
Step.	Heat Taken in.	Work Done.
A to B	$a + d$	0
B „ C	$b + e$	0
C „ D	0	$a + b = h + i$
D „ A	$-(f + e + d)$	$-f = -(i + j)$
	$a + b - f$	$a + b - f = h - j$

The area of the $\theta\phi$ cycle would be, as before, $a + b + c$, but the $p v$ cycle would be smaller by the strip $c + f$. If the lowest available temperature is raised, it does not reduce this difference, as it is on both sides of the line of the lowest available temperature.*

Turning back to Fig. 8, cutting off the area by the curve I K L does not make the efficiency higher, according to the $\theta\phi$ diagram, though the waste is the difference of areas of the $p v$ and $\theta\phi$ cycles, and though cutting off this corner lessens the $\theta\phi$ cycle. If the path had been by I J L, the steam would have been expanded further, and more work would have been obtained. If the expansion from I to J and the compression from J to L were reversible, both $p v$ and $\theta\phi$ cycles would be equally enlarged by the

* For simplicity it is here assumed that at the lower temperature $U = d + e$; it is in fact a little less. This does not reduce the area $c + f$, so the proof is not affected by the slight inaccuracy of the assumption.

course taken. In cutting off the corner what is really done is to increase the waste by raising the lowest available temperature. This is another form of the same thing as occurred from G to H. Thus at I the waste so far incurred is e , part of the area



N I J M being still to be had as work; but if the exigencies of the case call for a raising of the lowest available temperature, there is a reduction of the efficiency of the engine, and an increase of the waste, but not an increase of difference of cycle areas. The corner area I J L K is not ungained work in the

sense the term has been employed ($\int \theta d\phi - h$), due to irreversibility; it is increased waste due to raising the lower temperature limit.

The irregular area $b + c + d + e$ is the total reversible waste, assuming that the entropy from H to I was increased by some of the heat given out between F and H. It must not be supposed, however, that the waste is necessarily no greater than this.

So far irreversible compression has not been discussed. If a cylinder of gas or steam is compressed by using up external work, it is difficult to think of any form of irreversible compression which would use up more work and give out more heat than would account for the decrease of the steam's entropy. In a turbine acting as a pump, however, the waste would be considerably greater than the area under the $\theta\phi$ cycle. This is pointed out to prevent any such mistake as supposing the area under the $\theta\phi$ cycle to be the only waste. The waste must be at least that area, and it may be more. This increased waste appears, however, as a reduction of the $p v$ cycle area, as the increased waste due to irreversible compression increases the work put into the working substance by raising the lower side of the $p v$ diagram's cycle. It thus shows the difference of area of the $\theta\phi$ and the $p v$ cycles. The excess of area of the $\theta\phi$ over the $p v$ cycle is thus made up of two parts: the ungained work, due

to irreversible expansion, and lost work, due to irreversible compression.

In practical engineering, in the case of a reciprocating engine, we have some approach to the $p v$ diagram given by the indicator; but there is uncertainty as to the value of v at the beginning of the stroke—that is, until the admission is finished. Again, there is uncertainty if the exhaust opens gradually. Moreover, the steam may not be at the same temperature throughout its volume at any given time. An approximately true $p v$ diagram is made, and the $\theta\phi$ inferred from it by means of tables or Sankey's chart. The difference of areas of the cycles should then be measured, to give the ungained work, and the wasted work, and the lower boundary of the cycle should be examined to see whether the waste can be reduced anywhere by keeping down the lower temperature limit.

Ungained work due to irreversible expansion in the cylinder is too minute to matter in a reciprocating engine, but in the turbine it may be a very serious matter. The steam turbine may in the future be very much more carefully studied thermodynamically than the reciprocating engine. But there is a good deal of ungained work in an ordinary engine in wire-drawing through valves and ports.

The $\theta\phi$ cannot well be compared with the indicator diagram in the case of a turbine. It is in fact somewhat difficult to find out what is going on

inside the case. If it is driving a dynamo the output and the steam supply are known and the pressure, temperature, and dryness, of the steam as it enters. The temperature can be taken by inserting small thermometers or thermo-couples at various points. The velocity may be not great enough to prevent the pressures being taken from point to point; and perhaps some conclusions as to the dryness at various vanes can be obtained.

If the condition of the steam entering is known, and the temperature of the condenser, the maximum or ideal efficiency is known, and an ideal $\theta\phi$ diagram can be plotted. If the turbine is jacketed the jacket steam must be included. From the pressure temperature and wetness of the exhaust steam, its specific entropy can be found and marked on the $\theta\phi$ curve, and an equivalent exhaust curve drawn, as in Fig. 8. If the turbine, whether jacketed or not, does not lose heat perceptibly by radiation and convection, the state point for the exhaust will be to the right of that for admission, and lower in temperature of course. From the diagram so obtained the "ungained work" can be found. The inefficiency will be the result of irreversible expansion, and conduction of heat along the metal-work of the turbine. This tells the result of the whole turbine, and when several turbines are used in series that is specially valuable, corresponding roughly to the information as to each of the

cylinders in a reciprocating engine. If the necessary information can be obtained from point to point throughout the turbine, the localisation of blame is possible, and the designer can find out where the steam is rushing through too easily without doing its proper work.

Into the details of the application of the $\theta\phi$ diagram to actual practice it is not my object to go. That may be left for a future opportunity, or the work may be done better by others. But the first thing is to get the theory of the $\theta\phi$ diagram cleared of the common errors about it, so that its real meanings can be brought out.

The present position of the $\theta\phi$ diagram in engineering is that it is discussed in college text-books and in treatises for engineers; and it is said to be very instructive, and to give great insight into the economy of the steam-engine. But it has made little or no progress in real engineering. One engineer, of high rank, has been said to have used it, and got benefit from it. But so long as it is supposed that entropy is $\int dh/\theta$, or heat-weight, or a factor of heat, or that the $\theta\phi$ is a heat diagram, or that its area is in British thermal units, or that the $\theta\phi$ diagram is of the same area as the $p v$ cycle, it seems likely to remain practically useless. It will be treated with great respect, because people always respect what they do not understand, especially if it looks at all mathematical. Engineers

will not like to admit that they do not understand it; or, at most, those who have neglected mathematics will regret that the calculus was not taught apprentices in their young days, and recommend young men to take the $\theta \phi$ diagram to their bosoms and thank their stars for it. They may even tackle one of the numerous and excellent books of potted mathematics with which the benighted engineer is now befriended. If they can digest the potted mathematics with any sort of comfort, they are certain to be saddened internally by the $\theta \phi$ diagram as at present constituted. But they feel it is a wonderful thing, which ought to be swallowed.

CHAPTER IV.

CONDUCTION.

Movement of Entropy.—When one body is in contact with another and loses heat to it, it is usual to say that the heat moves from the hotter to the colder body, just as if the heat were caloric, that moved from one place to another. But what really happens is that the heat of one body increases as the other diminishes. Similarly, energy is said to move. Light, electricity, sound and waves on water are all regarded as moving. When a body is in contact with another, and decreases its entropy at the same rate as the other increases, it is most convenient to think of entropy as moving from one to the other, just as we think of heat moving. As the entropy of a body cannot decrease without heat coming out, while it can be increased without heat coming in, it is easy to think of entropy as moving from one body to another, and as increasing or growing in any body, but never as disappearing. Thus entropy may move, and may grow, but never disappears. There are sources, but no sinks. I do not know if entropy is considered as moving in any treatises on thermodynamics, but think

not; but that does not make the idea any less useful or valuable.

Conduction of Heat.—Conduction of heat is a very important irreversible process. Suppose a hot body, say a vessel containing 10 lbs. of water at 650° F.A., its entropy being 2.79, is put in contact with another of the same size, but at a temperature of 550° F.A., its entropy being 1.09, the two will come to the mean temperature of 600° F.A., and their entropies will be 1.97 each, or 3.94 together.

The total entropy has thus gone up from 3.88 to 3.94, showing incurred waste of 0.06 multiplied by the lowest available temperature. Suppose the lowest available temperature to be 550° , the waste is thus 33 British thermal units.

If the 10 lb. of water at 650° were put in connection with a thermodynamic engine which could take heat at a gradually falling temperature and return the waste heat at 550° , a certain output in work would be obtained. Of course the water cannot give out all its heat at 650° ; the mutivity $(\theta_1 - \theta_2) \theta_1$, or changeability of the heat into work, falls with the temperature. The water loses as much heat between 650° and 600° as between 600° and 550° , but more of the heat given out between 650° and 600° is convertible into work. If one vessel gives heat to a thermodynamic engine from 650° down to 550° , there will thus be more work obtainable than if two gave out heat from 600° to 550° .

This is shown clearly by the $\theta \phi$ diagram. Fig. 12 is the $\theta \phi$ diagram for 10 lb. of water from 550° to 650° F.A. The area A C F I represents $U_1 - U_2$, or U at 650° F.A., taking 550° as zero. It is obviously equal to 10×100 , or 1,000 British thermal units. The available part of the energy is

$$W = 10 \int_2^1 \frac{\theta - \theta_2}{\theta} d\theta = 10 (\theta_1 - \theta_2) - 10 \theta_2 \log. \frac{\theta_1}{\theta_2}.$$

The first term is the whole of the heat needed to raise the temperature from 550° to 650° , or 1,000 British thermal units, and is shown by the area A C F I. The second term is the waste A D F I, for $A D = \Phi = 10 \log. \theta_1/\theta_2$, and θ_2 is I A. So the available part is the area A C D. If a vertical line B G is drawn so that $G B = 600^\circ$, A E is the entropy of 10 lb. of water at that temperature, taking 550° as zero; and A B G I is 500 British thermal units. One vessel of water thus has the heat A C D available or convertible into



work to start with, while the other has none. On equalising temperatures there are two vessels, each with only A B E available; and A C D is obviously greater than twice A B E. As the area A B G I is equal to B C F G, A E is greater than E D, so the entropy A D of the vessel at 650° is less than that of the two vessels at 600° , or twice A E,

and the waste, twice $A E G I$, is greater than $A D F I$.

When a hot body communicates heat to one of a lower temperature, there is thus incurred waste or increase of entropy of the two. Earlier in this book reversible changes have been discussed in which heat went from a reservoir to a perfect gas and expanded it, and so on. The provision was made, however, that the difference of temperature was sensibly nothing, so as to give no perceptible down grade of temperature, and no increase of entropy due to irreversible conduction.

It has been shown that if a hot and cold body are put in contact with each other and allowed to equalise their temperature, there is a growth of entropy; but only the final result has been considered. It may be as well to discuss what happens during the change. Suppose a reservoir of heat—that is to say, an ideal body so large that it can give out heat without falling in temperature—is put in contact with, say, a mass of iron at a lower temperature. Suppose for the moment that the conductivity of the ideal body is so enormous that the part of it against the iron remains at the same temperature as the rest of the reservoir, say θ_1 . The face of the part of the iron block touching the reservoir is then at temperature θ_1 . If the block, to begin with, is all at uniform temperature, as soon as contact takes place the block is at θ_1 on one face, and at lower

temperatures elsewhere, and the temperature of the block is no longer uniform. In a given time the reservoir has lost heat, say H_1 , at constant temperature θ_1 , so its entropy has been reduced by H_1/θ_1 . The block has received heat H_1 at θ_1 , as θ_1 is the temperature of the face or part of the envelope through which the heat H_1 passes, so its entropy increase, as far as heat from outside is concerned, is H_1/θ_1 . But at the end of the process, when the block has come to temperature θ_1 , and taken in H_1 , its increase of entropy is greater than H_1/θ_1 . There has been a growth of entropy in the volume of the block. This volume growth is evidently the uncompensated entropy due to the irreversible nature of conduction. If the block takes in heat H_1 at temperature θ_1 , its increase of entropy is thus greater than H_1/θ_1 ; and if the temperature of the face varies during the change, the entropy taken in is $\int dH/\theta$ —the compensated entropy; but the entropy of the block is greater than $\int dH/\theta$ by the uncompensated entropy, or $\Phi > \int dH/\theta$, as in all irreversible or real changes. It must be borne in mind that θ is the temperature of the face of the block in contact with the reservoir, not the temperature of the block. The temperature of the block varies from part to part. To find how the entropy grows during conduction, imagine a bar of, say, copper of uniform section, say, a square inch. Let it be kept hot at one end and cold at the other, and be wrapped in

heat-insulating lagging along its length. Imagine a surface cutting this bar across so that all this surface is at one temperature θ_1 . The copper on each side of this surface is either hotter or colder, but the surface is at θ_1 , and remains at θ_1 , because the copper is in a steady state, with heat flowing along steadily and continually at uniform rate. An inch along toward the colder end imagine a second surface to cut the bar at right angles, and let its temperature be θ_2 . Let θ_1 be 132° Fahr., and θ_2 be 32° Fahr. Then the flow of energy, calculated from the thermal conductivity of copper, is about 0.5 British thermal unit per second. Through the hotter face we thus have each second $H=0.5$ and $\theta_1=593^\circ$ F.A., so there is an intake of entropy of 0.00083 per second. At the cold face there is an outflow of $H = 0.5$ at $\theta_2=493^\circ$, and the outflow of entropy per second 0.00103. There is thus a volume growth of entropy of 0.0002 per second in the cubic inch of copper. If freezing-point is the lowest temperature, the waste due to the irreversibility comes out at 0.14 British horse-power.

Whenever there is conduction of heat there is thus growth of entropy throughout the volume of the conducting body. Thus the fall of temperature between the immediate surface of the hot coal and the water is all by continuous temperature gradients—that is to say, by conduction.

There is great growth of entropy in the furnace

gas between the spot where the conduction takes place, and the boiler flues or tubes. There is growth of entropy in the external scale or dirt; a little growth in the metal separating the gases from the water; considerable growth in the scale. Boiler scale is a sort of entropy hot-bed. There is more growth of entropy in conduction in the boiler; but this is not serious. Then there is growth in the metal of the valve that separates steam at different temperatures. The growth of incurred waste in a large slide valve, such as used to be employed in marine engines, may amount to about 10 British horse-power, though there is no loss of heat. Then there is waste in conduction from the jacket to the cylinder, from the steam to the metal walls and back again, and so on. All this growth of entropy means waste of energy that it is the engineer's object to keep down. All this entropy has nothing to do with the waste of heat by radiation and conduction. When heat is radiated from a pipe, for example, at the rate of, say, enough British thermal units per second to amount to 10 British horse-power, whatever that number may be, it does not deduct 10 British horse-power from the engine output, because the engine would only have used some of the heat anyhow.

The growth of entropy in conduction of heat is not generally treated in this way; in fact, the method may be original. Writers on thermodynamics—

even specialists—do not usually give any indication of what they mean by θ or p in irreversible changes. In discussing conduction in reversible changes, θ is the temperature of the reservoir or of the working substance, or both, as it is the same, and the entropy equation is $\int dH/\theta = \Phi$. Then in the case of irreversible change we are frequently told that $\int dH/\theta = \Phi$ is still true, which is nonsense anyhow, or that $\int dH/\theta < \Phi$, which is vague if we are not told what θ is. There may be no reservoir, as the heat H may come from a body whose temperature is not uniform. If the working substance is also of varying temperature, θ cannot mean the temperature of the working substance. Personally, I have always read θ to be the temperature of the bounding surface through which the heat H passes, as that is the only reading which conveys any physical meaning to me; but I have since found I am rather peculiar in this. What idea is conveyed by $\int dH/\theta < \Phi$ to those who do not think of θ as the temperature of the bounding surface I cannot conceive. There seems to be a large class of people who are mathematically trained only to the point of having facility in the blind manipulation of mathematical symbols, and they have the extraordinary faculty of being able to read, and even write, mathematical symbols, and to get correct results without having any clear idea of what they are doing. Of course, this involves a very degraded

type of mathematics. Sometimes it is held that θ still means the temperature of the conducting body, and the body must be split up into elements each so small that its temperature is sensibly constant. Thus, if there are two bodies at different temperatures, but each at uniform temperature throughout, the hot one may give heat slowly to the cold one. When they are equalised, the total entropy has increased. Of each it is true that $\int dH/\theta = \Phi$, where θ is the temperature of the body. It is, therefore, it is said, true of each element of a body, if the body is not at uniform temperature; but the elements are so small that each is at a uniform temperature, so that for the whole body $\int dH/\theta = \Phi$. Of course, this is dreadful confusion; H and θ have different meanings in the two cases. The underlying idea is also confused. If a hot and a cold body are each at a uniform temperature, and the hot gives up heat to the cold, there must be something between them in which the conduction of heat and temperature gradient takes place. That something, in a given time, takes in H at θ_1 and gives out H at θ_2 , if not itself absorbing or giving out heat. The entropy growth is therefore going on in it. The growth goes on when there is conduction of heat and a down grade of temperature; and to assume that a conducting body can be divided up into elements, each uniform in temperature, involves the body being made up of something like

the bricks of a house with badly conducting mortar between them. The mortar may be thinned without limit, but if the down gradient of temperature is there and a flow of heat across, the uncompensated entropy grows entirely in the mortar. To neglect the mortar is to make out that a body conducting heat is made up of elements, each of which is undergoing a reversible change, while the whole undergoes an irreversible change. The argument is like saying that a path down a hill can be divided up into elements so small that the height of each is uniform. Water running over each, therefore, does no work, so water running down the hill does no work. This point is emphasised here because it is not generally realised that there is a volume growth of uncompensated entropy wherever there is a temperature gradient. This is a very convenient idea, as it shows that all conduction or radiation of heat involves waste, the power wasted depending solely on the temperature and its rate of decrease, and the conductivity of the material.

The Unit of Entropy.—Nomenclature is one of the weak points of thermodynamics. There is no name for the unit of temperature, and there are two thermometer scales used in England and two on the Continent. None reads exactly in accordance with the Kelvin or perfect gas scale. The unit of heat, which is quite an unnecessary nuisance, has no name, for British thermal unit is not a name; it is an

opprobrious epithet. The unit of entropy has not even that. It might be called the British entropic unit. I have elsewhere used the term "entrop" to denote the unit, also the term "claus," short for Clausius, for the practical unit of entropy on the C.G.S. system. It is usual to derive the practical unit on the C.G.S. system from a man's name, as the Ohm, Volt, Joule, &c. The claus is the entropy which, when multiplied by the lowest available temperature in absolute Centigrade degrees, gives the incurred waste in joules, not in calories, either of the big kind or of the little kind, or of the middle-sized, if there is one yet. The British entropic unit, as used in this book, is the entropy which, when multiplied by the lowest available absolute temperature, gives the incurred waste in British thermal units. "Entrop" is shorter and more convenient than "British entropic unit." It does not matter which thermometer scale is used in the case of the entrop, for if a body—say 10 lb. of water—at the temperature of boiling water has 3.14 entrops—the waste, if all the 180 British thermal units are given out at freezing temperature, will be 180 by 3.14 British thermal units. But if degrees Centigrade are used, there will only be 100 thermal units, whose nationality it may be difficult to get any civilised country to acknowledge, so the waste will be 100×3.14 , which is the same heat as before. The claus refers to absolute Centi-

grade degrees only, as the alteration of the thermometer scale, though it would change the magnitude of each of the various calories, would not affect the joule.

It may seem strange that a standard state has to be taken for zero entropy, instead of simply finding the total entropy of a body and stating it. The usual reason given is that the total entropy of a body is unknown. The real reason is that the entropy of a body is necessarily infinite.

If a body of unit mass is imagined at zero temperature, and that is taken as zero entropy, because as no heat can be given out no further reduction of entropy is possible; to heat it up to any finite temperature θ , the increase of entropy necessary is $\int_0^1 d\theta/\theta = \phi$. So $\phi = \log. \theta_1 - \log. \theta_0$; but $\log. \theta_0$ or $\log. 0$ is negative infinity, so the entropy needed to raise the body to any finite temperature is infinite.

Physical Meaning of Entropy.—So far entropy has been treated as a function of the co-ordinates, or of the incurred waste; but the question arises as to whether it has any further physical meaning. For instance, if a body is heated, we picture the change of temperature as being accompanied by change of molecular motion. The difficulty with entropy is that it is a quantity whose increase denotes incurred waste, and it is thus very general, so that entropy is increased in different ways in different cases, and

there is no one molecular change that corresponds with increase of entropy.

Take first the case of a perfect gas. The temperature there corresponds with the kinetic energy of the molecules. Suppose, for simplicity, the molecules or atoms are all moving at the same speed, and their total kinetic energy is the same as in the perfect gas, with its molecules at various speeds, the equivalent uniform speed may be called the "equivalent speed." It is not the mean speed, because kinetic energy varies as the square of the speed. Then if the gas is heated at constant volume, the entropy varies as the logarithm of the equivalent kinetic energy, or of the square of the equivalent speed. In this case the entropy increases as a function of the heat of the gas. Suppose now the gas is expanded isothermally, its internal energy and equivalent speed remain the same as before, but the entropy increases as the logarithm of the volume. This has nothing to do with the kinetic energy of the molecules or equivalent speed, as they are not altered. What is altered is the infrequency of collision and the mean path, both in the same sense and to the same degree. The entropy is thus proportional to the logarithm of the length of the equivalent free path of the molecules. Thus when a perfect gas is compressed adiabatically, its entropy is not increased, though it gets hot, as the increase of the logarithm of the square of the equivalent

speed is exactly balanced by the decrease of the logarithm of the equivalent free path.

In heating a substance which undergoes no physical change, such as a solid, the entropy is again proportional to the logarithm of the square of some sort of equivalent molecular speed. When the solid melts, or a liquid vaporises, there appears to be some change of kinetic energy by regrouping the parts of the moving systems so that they still communicate the same energy to neighbouring bodies by battering them, but have some additional energy, such as of rotation, which is not communicated by battering. The entropy increase of physical change is thus still proportional to the logarithm of the square of an equivalent speed.

One reason why there is obscurity as to the physical meaning of entropy is that it is treated in orthodox thermodynamics as one quantity. Some heterodox observations here may do no harm. Entropy is really the sum of several quantities. In the case of a pound of a perfect gas increasing its entropy by being heated at constant volume, the increase of entropy is proportional to the logarithm of the equivalent momentum of the particles. That is one distinct quantity, which I have called χ_s , or the quantity factor of sensible heat. If a pound of ice is melted, the increase of entropy is again the logarithm of some equivalent momentum. This quantity I have called χ_p , or the quantity factor of

latent physical heat. What is often called the disgregation energy of evaporating water, that is to say, the increase of internal energy not including any external work done, is thus $\theta \chi_p$. If chemical work is done by taking in heat, its quantity factor is χ_c , where χ_c is, again, the logarithm of some equivalent momentum of the particles forming the new combination. Return now to the perfect gas, and let it expand isothermally. It increases in volume, and the increase of entropy is proportional to the logarithm of the volume. We thus have χ_s , χ_p , χ_c , and a function of the expansion which may be called ϵ , which is proportional to the logarithm of the volume. The increase of entropy is the sum of these four, or

$$\phi = \chi_s + \chi_p + \chi_c + \epsilon.$$

We need not consider chemical changes here, so we have

$$\int \theta d\phi = \int \theta d\chi_s + \int \theta d\chi_p + \int \theta d\epsilon.$$

Uncompensated entropy thus occurs in engineering in two ways. If heat is conducted from a hot to a cold body the bodies average their energy up. This means increasing the equivalent momentum of their particles. Thus, if a shot going at 2,000 feet per second and another at 1,000 were to collide and glance off at equal velocities, so that the total energy remains constant, as the initial energies are as 4 to 1, the final energies are $2\frac{1}{2}$ times that

due to 1,000 feet per second, or the speed is as the root of $2\frac{1}{2}$, or nearly 1,600 feet per second, instead of 1,500, which would be the average speed. The momenta before collision were as 2 and 1, the sum being 3, whereas after collision the sum is in proportion of $3\cdot2$. In averaging up their energy by conduction of heat there is thus an increase of equivalent momentum, and the logarithm of this is the increase of χ_s or of ϕ , as far as conduction goes. This increase is obviously uncompensated, corresponding to an irreversible change. It is clearly impossible to reduce this equivalent momentum by making one part hot and the other cold again without taking in heat at a high temperature and giving it out at a lower, that is to say, the change incurs waste.

When the perfect gas expands isothermally, whether it does external work or not, it is only changed as regards the free path of its particles, but to bring it back to its original state needs compression by external work, and if a particle rebounds from a wall that is approaching it, it increases its velocity, so that if the compression is to bring the gas back to its original state, heat must be given out and work taken in, that is to say, there must be degradation of work into heat, of which a portion must be waste.

Thus χ and ϵ have this in common, that their increase means that to get the substance back to its standard state, even reversibly, involves giving out

heat. When a gas expands isentropically its increase of ϵ is exactly balanced by its decrease of χ , as it cools, and the entropy remains constant. Splitting entropy up into the sum of a number of quantities which have nothing in common except their relation to waste is new and unorthodox; but if the reader wants to have a physical idea of entropy I believe it is quite necessary. In thermodynamics the entropy is a sum of quantities having only one property in common, and has therefore no single physical meaning except as regards the results of its increase.

It may be urged that it is highly artificial for χ and ϵ and their sum ϕ to vary as the logarithm of the equivalent momentum, the logarithm of the volume, or free path, and so on; whereas volume and momentum are factors of energy. The answer is that we have by a pure accident taken temperature so that it varies as the square of the equivalent velocity of the particles. If we take as the tension factor τ , so that $\tau = \sqrt{\theta}$, and π as the corresponding factor of heat, we get π_s , π_p , and π_e , varying, not with the logarithms of momentum, but with the equivalent momentum; and η , corresponding with ϵ for the expansion function, which varies directly as the volume, and not as its logarithm. Splitting up heat into factors, and abolishing the idea of entropy except as the sum of the quantity factors and the expansion function

will, I feel convinced, make the study of thermodynamics more simple.

Conclusion.—Though everything in this book is, I believe, consistent with modern thermodynamics, the whole method of treatment is practically new. It has, as far as possible, been pointed out when anything may be unorthodox, so that the reader who is new to the subject may be on his guard.

As far as possible, I have tried to put a difficult matter in plain English, and not in mathematical symbols. This is a very thankless attempt, for if one were to succeed in making a difficult subject appear clear and simple, the reader would think the subject itself easy, or that it has only been treated in a very elementary way, and very often that the writer's knowledge is also equally elementary, perhaps untrustworthy. The same subject treated in an involved way, with a quantity of obscure mathematics—a first-rate man's mathematics are always clear, however, and his writing as simple as the case allows—is supposed to be more advanced and deeper, and to have much more in it.

Few realise that ease of reading varies inversely about as the square of easy writing, and if one wants kudos, the right thing is to make the subject as complicated and difficult as possible, and especially to use as many mathematical symbols as can be crowded in. It is quite the correct thing in science,

after making calculations, to “remove the scaffolding,” that is to say, to publish without giving the intermediate steps, so that others should think the feat greater.

In dealing even with an old subject in a novel way, which involves criticism of existing methods, it is necessary for a writer to rely on his own reasoning from step to step, as he cannot rest on others whose way is different, and, in his opinion, inaccurate. It is therefore most likely there are many slips and false steps in this essay. I am not young enough to be at all infallible; one would have to be very young indeed to be infallible in thermodynamics, which is perhaps the most slippery branch of science there is. It is hoped anyone who notices any slips will write to me, and advantage will be gratefully taken of any corrections or suggestions, if a second edition should be demanded.

APPENDIX.



THE REVERSIBILITY OF THERMODYNAMICS.

A NEW way of looking at an old subject can do no harm, and may do, and generally does, a great deal of good. In this appendix it is submitted that the ordinary discussion of the science of thermodynamics makes the subject unnecessarily obscure, and leads to all sorts of errors; and my object is to urge a different treatment which, it is hoped, will make the science more easily understood.

There is no branch of physical science so commonly misunderstood, not only by students, but also by scientific men of considerable standing, as thermodynamics. Some time ago I asked an eminent authority on the Continent to join in a discussion on entropy which had arisen out of a note to the presidential address I had the honour of delivering before the Institution of Electrical Engineers. He replied that though I was quite right in my statement that most writers on physics had got hold of a wrong idea of entropy, the matter was merely pedagogic, and therefore he would not

discuss it in print. A question of pedagogy would be outside the province of an engineer ; but as it is not really a question of method of teaching young men at colleges, but of giving clear ideas to scientific men who are not specialists in thermodynamics, the subject is of real scientific importance ; and I willingly acceded to the request of the Committee of the Mathematical and Physical Section of the British Association to open a discussion on thermodynamics, and this appendix consists essentially of the paper written for that purpose.

Present or Orthodox Treatment.—The study of thermodynamics suffers from the historical development of the science. During the first half of last century the principle of the conservation of energy was on its trial, and, though he soon discovered his mistake, Carnot had supposed that in his cycle as much heat came out of the working substance as went in. I pretend to no knowledge of the history of thermodynamics, but it looks as if Clausius, realising that the heat is not conservative in a Carnot cycle, found a function S , which is. Then came the question of the second law and the best way of formulating it, and the whole discussion centred round the Carnot cycle with dQ/T a complete differential. Instead of S , Q and T , I have used Φ , H and θ in this book, as Q is generally used in other branches of physics for the quantity factor of energy, not for energy, and T for kinetic energy ; and if Φ is

used for entropy, θ may well be used for temperature, as by Rankine, Maxwell and others.

The first matter generally is to state the law of the conservation of energy and to define "heat." Here there is a complete failure. The definitions and explanations really come down to saying in a more or less roundabout and complicated way that heat is what makes things hot. In its way this would be quite a nice and all-sufficing definition, but it is not adhered to at all. The domination of a name comes in. The increase of internal energy necessary to produce a change of (physical) state, such as melting ice, was called heat before thermodynamics began. Objectors to the caloric theory, I think, refused to call this energy heat, in order to annoy their opponents; but when the caloric advocates disappeared by dying out, or perhaps even by being occasionally convinced, increase of internal energy became latent heat again; and then the increase of internal energy and external work together became "latent heat," having a symbol C_p or K_p to itself, so that increase of U where there is no chemical change is heat, and the external work done per degree rise of temperature is part of the latent heat of the body, so the definition goes by the board, and heat that makes things hot is called "sensible," perhaps as a stigma on the other kinds of heat. The definition of heat is thus wanting. I will quote from some correspondence I had with one

of our leading mathematical authorities on thermodynamics. "What is wanted is a definition of *heat*. Can you define *heat*? If you can give a definition which will make it perfectly *clear what is heat and what is not heat*, you will be doing good work. But you must cover all possible cases." The italics are his. Now what does my correspondent want? There are two classes of definition in science. One is a mere verbal distinction which fits pre-existing ideas and conveys no information. For instance, everyone of my readers has, no doubt, a perfectly clear idea of what energy is, and also knows what is energy and what is not, in any given case; but to define energy so as to convey any information to anybody who has no pre-existing notion of it is no easy task. But perhaps what he really meant was something like this. "Is latent heat, heat? Surely external work is not heat. Is chemical energy heat? How far is radiation, thermal or luminous, heat? Are electron flights ever heat? If so, when are they kinetic energy, and when heat? When are electro-magnetic waves heat? Is the energy of pedesis heat? If so, and the little particles are made to jolt bigger particles, and so on till they finally shake lumps, is that heat or directed kinetic energy, and where is the line of demarcation? At what stages in the electrostatic or electro-magnetic hysteresis cycles does the entropy increase?" I do not know whether a definition which would answer these questions would

satisfy my friend, but some such definition is wanted. Many of these questions are, no doubt, answered by inference in papers on those particular subjects written from a thermodynamical standpoint; but an ordinary treatise on thermodynamics does not touch them, or answer my friend's question in the least.

Then there is a difficulty about thermometry. The Fahrenheit scale takes the expansion of mercury one-hundredth per cent. as a "degree," the Centigrade divides the difference of two arbitrary temperatures into 100 parts, and is therefore regarded as more scientific, and the Réaumur exists in real life but not in science. Much trouble is therefore devoted to elucidating Kelvin's scale, and it is then generally assumed that the Fahrenheit and Centigrade thermometers read in the Kelvin scale, only with different zeros and different units of temperature. The main point to which attention is especially directed, however, is, that writers are so eager about showing that production of work means disappearance of heat, and so anxious to explain Kelvin's scale and to discuss the second law and Carnot's cycle, that they discuss the whole subject only in connection with ideal reversible changes. Then the fact of dH/θ being a complete differential in reversible changes is very attractive to many people, because they can then get a lot of undeserved happiness in stringing together partial

differential equations tracing the relations of every conceivable thermodynamic quantity with every other, down to the most remote cousinships. Thermodynamics is thus apt to degenerate into nothing better than an exercise in differential equations.

In discussing the principle of entropy, the entropy of the working substance is treated almost exclusively, and that in connection with reversible changes and cycles alone. Irreversible changes are discussed as a sort of curious exception, but only very slightly. In many cases two bodies are considered before and after equalising their temperatures, and their increase of total entropy is discussed, but there is no explanation of how the entropy increases; only the initial and final stages are considered.

But the chief ground of the accusation I have the honour to bring is that anxiety to discuss the Carnot cycle and its bearing on the second law, and to work with a quantity Φ which could be assumed conservative, has led to a very elaborate mathematical development of the theory of reversible changes, and has relegated real thermodynamics to an undeserved background.

My historical notions may be wrong, but it looks as if Clausius, when Carnot's reasoning had been vitiated by his original mistake as to conservation of heat, looked for something that was conservative in the Carnot cycle and found entropy. He got the "tropie" from the Greek, and put on the "en"

to make the word sound something like its conservative analogue "energie." Then in discussing real changes he found that entropy is not conservative, and founded the principle of modern thermodynamics, that the entropy of the universe strives to increase; a principle which is the very backbone of the science. In spite of this, the ordinary treatise, though it mentions Clausius's principle, and perhaps touches on Kelvin's work of the same period, says very little about it. By "ordinary treatise," I need hardly say, I do not mean to include such works as those of Planck or Duhem, or those written by the abler modern physical chemists.

Entropy is defined with reference to reversible changes only by the equations

$$\int dH/\theta = \Phi \text{ and } (\int) dH/\theta = 0,$$

which give no sort of notion what entropy is, and which are only numerically correct in the case of reversible changes and cycles respectively, and, in fact, are never even numerically true. The foundation of thermodynamics is that neither of these equations is true. I know of no writer who has tried to give any sort of explanation of what is meant by entropy, except that it is the quantity factor of heat, which is obviously nonsense. It is not meant that specialists on thermodynamics do not understand their own subject or write inaccurately; my complaint is that the treatment of thermodynamics is obscure and

misleading, and has lead to great confusion and much error.

Nearly all writers on physics, for instance, define entropy by the equation $dH/\theta = d\Phi$, or its equivalent. That is to say, they are led to suppose that what would be true if there were any reversible changes is true in fact. dH/θ , or $d\Phi$, is treated as a typical complete differential. An adiabatic change is supposed to be isentropic. $(\int) dH/\theta = 0$ is supposed to be the second law of thermodynamics. Entropy is said to be a factor of heat, and so on, a whole tissue of errors and misconceptions thus arising from the impression given by looseness of diction. When any man of ordinary intelligence and the necessary training cannot understand what has been written, it may be taken for granted it is the fault of the writer. Generally, people are of an opposite opinion, perhaps thoughtlessly, and if the treatment of a subject proves to be puzzling, the author is rather to be admired for being master of such a difficult subject, and not blamed for not making it simple; whereas, if he put the matter simply and clearly, he would get but little credit for his work. This is especially true of subjects that can be treated mathematically; the scientific world has an immense reverence for anything put in mathematical language, though it needs much more ability and a clearer head to put it in words. Was it not Maxwell who said that mathematics is a shorthand, and that

anything that can be put in symbols can be put in words, if the writer really understands it? Nobody really understands unless he can express himself in words. Thermodynamics seems to be peculiarly unfortunate in being a vehicle for blind mathematics. It is not for a moment hinted that science cannot be clear if it is mathematical ; quite the reverse. The great writers on physics use mathematics in such a way that they are merely shorthand methods of explaining physical ideas. Any reader grasps the physical ideas at once, unless his mathematical equipment is too limited ; but even then he feels the physical ideas are there, and very often finds the study a good way of learning mathematics. On the other hand, another writer will make the simplest matter unintelligible by mathematical treatment. Thus such an expression as $\int dH/\theta = \Phi$ is a perfectly clear statement of fiction. But when we come to fact we are told that $\int dH/\theta < \Phi$. Now what does that mean? Being an engineer, in coming across such an expression I sought an interpretation that gave a physical meaning. θ could not be the temperature of the reservoir, because there may be no reservoir ; for instance, the body ceding heat may not be at uniform temperature, for example, in considering part of a conductor of heat where there is a temperature gradient. Then θ cannot generally be the temperature of the body because that is not usually uniform. To make sense, θ is the temperature of

the bounding surface, and H is a flux through the surface. But I find I appear to be rather peculiar in this interpretation. What then does the orthodox writer mean by H and θ in irreversible changes, and what idea is really in the mind of the reader as he glides over such expressions? That there is a tendency towards blind mathematics and fogginess of idea in thermodynamics is, I submit, proved by the inaccuracy of the terms used, the absence of named units, and the absence of physical ideas. How many chemists have any clear-cut idea of what the "Thermodynamic Potentials" really are?

The entropy principle was formulated half a century ago. Before and since then the question of what determines the direction of chemical action was eagerly discussed. The entropy principle was supposed to be familiar to every scientific man, but it was not assimilated in the least. After about twenty years the chemical puzzle was solved by Horstmann, who pointed out that the increase of entropy is the criterion. Rayleigh, doubtless independently, said the same in 1875; then followed Massieu, Gibbs, and Helmholtz. Rayleigh said it in plain English; the others, especially Massieu, said it in mathematics. But even that has produced but little effect, and now, after more than half a century, the principle of increase of entropy is by no means generally understood by chemists, nor by engineers,

though they are both exceedingly anxious to understand and use thermodynamics. This might be the fault of chemists, engineers, and other scientific men, but it seems much more likely to be due to obscurities in thermodynamics.

It is easy to get the reputation of a reformer by finding fault with existing conditions. It is more to the purpose to show what one thinks is an improvement by a specimen. I have, therefore, attempted a short elementary exposition, especially as far as it concerns mechanical, apart from chemical, engineers. This forms the body of this book. In this is exemplified a treatment of elementary thermodynamics, which depends largely on the reversal of the ordinary method. For instance, dissipation and waste are explained before reversibility and the Carnot cycle; entropy is defined without any reference at first to heat passed into a body; the increase of entropy is treated as normal, and reversible changes as a purely ideal exception; the second law of thermodynamics is merged in the impossibility of perpetual motion; the entropy of the universe and of the isolated system is treated before that of the working substance; and the growth of entropy during conduction is treated later. For that reason this essay is headed as it is. To put the matter succinctly, for easy grasp, a sort of sketch will now be set out, which also summarises the body of the previous chapters.

SKELETON OF THERMODYNAMICS.

Energy can be divided broadly and clearly into two kinds, which may be called work and heat. Different kinds of work can be converted one into another wholly in idea, and nearly wholly in fact; different kinds of heat can be converted wholly into one another. Work can be wholly converted into heat, but heat can only be partially converted into work if the converting substance returns to its original state, the rest of the heat being degraded into a less available form. This definition of heat includes the heat that makes things hot, and locomotive heat in general, and it also includes "latent heat" at constant volume, but only part of any misnamed "latent heat" that includes any form of external work. It includes latent heat of fusion, of vaporisation apart from external work, and of allotropic modification. What is most heterodox is that it includes chemical energy.

There are three classes of perpetual motion. They are all impossible, and two of them are not approximately attainable, but third-class perpetual motion is approximately possible.

First-class perpetual motion is when an otherwise isolated system can give out energy continually, or without decreasing its own. The impossibility of first-class perpetual motion, coupled with the impossibility of an energy sink is the principle

of conservation of energy, and gives the first law of thermodynamics.

Second-class perpetual motion is when an isolated system, in spite of friction or its equivalent, goes on continually. Second-class perpetual motion would not contradict the principle of the conservation of energy. Its impossibility is the second law of thermodynamics.

Third-class perpetual motion is when an isolated system—a mechanism, for instance—has no friction, or no equivalent of it, and therefore goes on or changes continually. The impossibility of third-class perpetual motion is the third law of thermodynamics. It is not called the third law, but it deserves that rank.

Waste.—Work is valuable to man, and the portion of any heat that can be converted into work, leaving the converting substance in its original state, is valuable; but the rest of the heat is waste. When work is degraded into heat, a portion of it is available as work, the rest is waste. The third law of thermodynamics states, in other words, that no change in nature takes place without incurring waste.

Definition of Entropy.—The increase of entropy of an isolated system, multiplied by the lowest available temperature, is the incurred waste. The waste, therefore, depends on the lowest available temperature and the entropy. As any given change can only increase the lowest available temperature

infinitesimally, the second and third laws may be stated in the form, "The entropy of the universe strives to increase." So does the waste. Its maximum will be reached when all heat is unavailable and there is no work left. The incurred waste increases faster than the entropy of the universe, because the lowest available temperature is always rising. The limiting expression "incurred" is used before waste, advisedly. Suppose, in an isolated system, some gas expands doing some work external to the gas. The heat of the isolated system is diminished, the work increased, and the total energy unchanged. The heat being diminished without any corresponding rejection at lower temperature, the waste portion is decreased. There is thus actual decrease of waste. But, to get the gas back to its original state, work must be degraded into heat again, and, according to the third law, there is then increase of waste. Had the process been reversible, there would have been no increase of incurred waste in the system, but, as far as the gas alone is concerned, its own increase of entropy multiplied by the lowest available temperature would be the waste involved in bringing it back to its original state.

When during a change the entropy of a body forming part of the system diminishes, the entropy of another part must increase to the same extent in an ideal change, and to a greater extent in a real change. In the ideal change the increase of

entropy of the body is called compensated, in a real change the part of the increase equal to the corresponding decrease elsewhere is compensated entropy, Φ_c , and the balance is uncompensated entropy, Φ_u , where $\Phi_u = \Phi - \int dH/\theta$.

When the heat of one body diminishes as that of another in contact with it increases, it is usual to say that the heat moves from one to the other. Similarly, when the entropy of one body diminishes while that of another in contact increases to the same or a greater extent, it is convenient to say the entropy moves and grows also. From the idea of the entropy of an isolated system and its increase in every change, it is easy to pass to the idea of the increase or decrease of the entropy of a body. In the case of reversibility the entropy of the isolated system is conservative, so that the discussion of the behaviour of any body or bodies may be treated as in dynamics, by examining the changes and inter-relations of the external co-ordinates; and the conservation of entropy, in the ideal case of reversibility, is a very convenient assumption, especially as it specially helps the treatment as in dynamics, the conservation of entropy corresponding with the conservation of energy. The exaggeration of the importance of this treatment has done much to foster incomplete understanding of thermodynamics.

By treating the increase of entropy of an isolated system as the fundamental idea and variations of

the entropies of the parts as derived ideas it is submitted that a much clearer notion is obtained. It is more convenient in practice, however, to consider the entropy of some substances or volumes which form parts of isolated systems. In this connection we have the following propositions:—

Reversibility.—A reversible change is an ideal change which could take place, with everything involved, in the other direction.

When a reversible change takes place in an isolated system there is no increase of incurred waste, for if there were, on reversing there would be decrease of incurred waste, and second-class perpetual motion would be possible.

When a reversible change takes place, therefore, the entropy of the isolated system remains constant.

A reversible cycle is a series of reversible changes which brings the working substance back to its original condition. The entropy of an isolated system is not altered by a reversible cycle being performed inside it.

In any reversible change, the total entropy of the system being constant, the increase of entropy of any part is compensated by an equal decrease of another part. The decrease of entropy of any body can only take place by a process which involves at least equal increase of entropy of the rest of an isolated system. Thus the entropy of a body may be reduced without its giving out heat by a thermo-

electric circuit, but that involves at least equal increase of entropy elsewhere in the electric circuit. Except in the case of a thermo-electric circuit, the entropy of a body can only be reduced by its giving out heat, for if it could be reduced by giving out work, there would be no corresponding increase outside, and second-class perpetual motion would be possible.

The reversible increase of entropy of a body can only take place by its taking in heat from outside (except by a thermo circuit), otherwise the entropy of an isolated system would be increased, and the change would not be reversible.

The entropy of a body, compared with its entropy in a standard state, is the entropy that must at least come out of it in bringing it back to its standard state; or it is a quantity which, when multiplied by the lowest available temperature, gives the waste portion of the heat given out in bringing the body to its standard state by reversible changes.

As the waste portion, or loss L , of heat given out through the envelope, H , is $H\theta_2/\theta_1$ where θ_1 is the temperature of the envelope, and θ_2 the lowest available temperature; and as by definition $\theta_2\Phi=L$, $\Phi=H/\theta_1$, or if the temperature of the envelope varies during the output of the heat H , $\Phi=\int dH/\theta$. Thus the entropy of a body in state B compared with state A is $\Phi_B-\Phi_A=\int dH/\theta$, where H is the heat that would be given out or taken in if the change were

reversible. The third law shows that in fact $\Phi_B - \Phi_A > \int dH/\theta_1$, the excess being uncompensated entropy Φ_u .

The entropy of a body thus depends on its state, and not on its past history.

Equilibrium.—If any small change imagined in an isolated system involves decrease of entropy, that change is impossible, in accordance with the second law. If it causes no change of entropy, there is equilibrium as far as that change is concerned, and no change will take place in either direction. If the change would increase the entropy, the change is possible and may take place, but only in that direction.

A possible change thus involves increase of entropy, or uncompensated entropy.

The uncompensated entropy of the working substances can be expressed in terms of the co-ordinates of each working substance alone, without other reference to the rest of the isolated system. Thus in the case of a working substance, where Φ_u is the uncompensated entropy, H the heat taken in, θ the temperature of the envelope, U the heat of the body, according to the definition given above, and W the external work done.

$$d\Phi_u = d\Phi - dH/\theta \text{ and } dH = dU + dW,$$

therefore $d\Phi_u = d\Phi - dU/\theta - dW/\theta$,

and if there is equilibrium,

$$d\Phi - dU/\theta - dW/\theta = 0.$$

If there is uncompensated entropy on making the change

$$d\Phi - dU/\theta - dW/\theta > 0.$$

The integral of this quantity is therefore written with the sign reversed and disguised under the name of a "Thermodynamic Potential," so that increase of uncompensated entropy decreases instead of increasing the quantity. Uncompensated entropy is a drawback, and thermodynamic potential is an advantage. It is with great respect to Professor Planck or Professor van Laar* that it is submitted that thermodynamic potential is a bad name for the function

$$U/\theta + W/\theta - \phi.$$

The third law shows that heat can never be changed into work to the extent it would be by a reversible cycle. The work that would be gained by a reversible cycle, and is not gained in a real change, may be called the "ungained work." Professor Duhem† calls it the "uncompensated work." The ungained work, $W_u = \int \theta d\Phi_u$, where θ is, if the working substance is of uniform temperature, the temperature of the envelope or body. If the temperature is not uniform, θ is the temperature of each volume element in which the uncompensated entropy grows, and integration is

* Or whoever is responsible for the expression.

† I think the term is originally due to Professor Duhem, but my memory may be at fault. See p. 70.

carried out throughout the volume; but as the expression is important only when $W_u = 0$, the meaning of θ otherwise does not matter for the moment.

If a small change involves decrease of ungained work it is impossible; if the ungained work is zero, the substance and its externals are in equilibrium as far as that change goes; if the ungained work is positive the change is possible, and may take place in that direction only. As the ungained work does not, unfortunately, exist outside the substance, nor anywhere else as work, it is best not to call it W_u , but Δ or D . Then, if the ungained work is zero during a proposed change, the "thermodynamic potential" is said to remain constant. If the ungained work increases, the thermodynamic potential is said to decrease. The ungained work due to a small change may be represented in terms of the co-ordinates of the working substance.

$$\begin{aligned} d\Delta &= \theta d\Phi - dU + dW \\ &= d\theta\Phi - \Phi d\theta - dU + dW. \end{aligned}$$

The external work, W , is general. It may be done electrically, or by expansion. If by expansion

$$dW = p dv = dpr - v dp.$$

Then $d\Delta = \theta d\Phi - dU + dW = d\theta\Phi - \Phi d\theta - dU + dW$

$$(1) \quad d\theta\Delta = d\theta\Phi - dU - dW$$

$$(2) \quad d\phi\Delta = -dU - dW$$

- (3) $d_v \Delta = \theta d\Phi - dU$
- (4) $d_p \Delta = \theta d\Phi - dU - dpv$
- (5) $d_{\theta v} \Delta = d\theta \Phi - dU$
- (6) $d_{\theta p} \Delta = d\theta \Phi - dU - dpv$
- (7) $d_{\phi v} \Delta = -dU$
- (8) $d_{\phi p} \Delta = -dU - dpv$

If the various partial differentials are taken as zero, the condition of equilibrium, and the right-hand terms, integrated without adding any constants, and reversed in sign so that their decrease corresponds with increased or ungained work, eight more thermodynamic potentials are involved. Part of No. 1 gives what is called "free energy." It is not energy, and is in no way remarkable for freedom of any kind. The results of three of these are the Gibbs's functions, which have been called, first by Professor Duhem, I believe, thermodynamic potentials, no doubt because they are constant for equilibrium, like potential in mechanics. Again, it is submitted with much deference, that the name is misleading. If the signs were not reversed, stabilities, or stability functions, might be a better name. In non-thermal reversible mechanics, equilibrium or maximum stability is reached when the potential is a minimum. Maximum stability can then be called minimum potential; but, surely, it does not follow from this that maximum stability is always synonymous with minimum potential, and that thermodynamic

potential is a synonym for the negative of stability, especially when applied to quantities that are not energy, though of the same dimensions as energy. Besides, the term potential is getting worn out. Counting the eight potentials just given as one specimen, I can think of nine kinds of potential used in physics, and a collector could doubtless find many more. They have various meanings and dimensions. Four or five of them belong to thermodynamics. If we have very many more potentials, the term may become a little difficult to define accurately and succinctly, though it is always impressive.

By defining entropy first in terms of the waste, and dealing with the increase of entropy of an isolated system first, and coming to the relation of increase of entropy to heat taken in reversibly later, the chance of confusing entropy with $\int dH/\theta$ generally, and supposing entropy is a factor of heat is avoided. This prepares the way for discussing the real factors of heat, such that $\int \theta dX = U$, where θ is the tension and X the quantity factor. In other branches of physics, not only $\int a db = W$, where a and b are tension and quantity factors, but where c is capacity for the quantity, so that $db/da = c$, $\int a c da = W$, or when c is constant, $W = \frac{1}{2} a^2 c$. In that case the tension factor is $\sqrt{\theta} = \tau$, and the corresponding quantity factor Π , so that $\int \tau d\Pi = U$. In a change where there is no external work done and no ungained work X is numerically equal to Φ , and is

the logarithm of the square of some sort of equivalent velocity of the particles. Thus in the case of a perfect gas the entropy depends on the logarithm of the square of the equivalent speed, and the logarithm of the equivalent free path of the particles of the gas if there is one, or of each if there are more.

The frequency of collision has to do with external work, and X depends only on the speeds. The physical meaning of τ and Π is much simpler; τ varies as the equivalent speed, and Π as the equivalent momentum.

Take the case of chemical energy as one of the forms of heat. U can be divided up into U_s, U_p, U_c for sensible, latent physical and chemical heat. $\int \theta d\Pi_s = U_s$; $\int \tau d\Pi_c = U_c$ and so on. At present heats* of combustion or combination are given in the lump. In the future we may have tables giving the θ and χ or the τ and π of each free element, and their change on reaction; or even their θ and ϕ . Then we would know beforehand in which direction each reaction would go. The question of the factors of heat need not be discussed here; it is a large subject by itself.

* This is another example of the extraordinary looseness of terminology that runs through thermodynamics. They ought to be caloric of combustion or combination, for the heat of fusion or vaporisation is the heat taken in during the change. The so-called heat of chemical change is given out during the change.

Heat Conduction.—If a body is conducting heat steadily, for instance, a uniform bar with one end kept hot and the other cold and no side leakage, the bar can be cut up into lengths by cross cuts imagined so that each cut is at uniform temperature. Let one be at θ_1 and the next at θ_2 , and let heat H pass per second. Every second H/θ_1 comes in and H/θ_2 comes out, so that there is a volume growth of entropy depending on the conductivity and the temperature gradient. Any body whatever which is not at uniform temperature can be divided up into elements bounded by two sides each with no temperature gradient, and a bounding surface parallel to the flow of heat, so that there is no passage of heat across. If the flux of heat is H joules per second, and $\theta + \frac{d\theta}{ds} d\theta$ and θ the temperatures of the two faces, the increase of uncompensated entropy per second, is $-\frac{H}{\theta} \frac{d\theta}{ds}$ per unit volume, and the ungained work is $-Hd\theta/ds$ per second, or the ungained power is $-Hd\theta/ds$ watts; $d\theta/ds$ being negative. Integration throughout the volume gives the total ungained power.

Units.—The fact that the units in thermodynamics have no names goes to show that the science is not fully developed. Measurement is an essential of science.

There is no name for the unit of difference of

temperature. Trigonometry and heat alone use "degrees." Marks or notches would not be less barbarous. Then there is no name for differences of temperature according to the absolute Kelvin scale.

The practical unit of heat, on the C.G.S. system, is the joule, but this is hardly ever used in thermodynamics. The calorie is a survival of the days when it was not fully realised that heat is energy. It involves an unnecessary and troublesome co-efficient, and people are putting big calories and little calories, and, perhaps, intermediate calories into circulation.

There is no unit of entropy. I would suggest the claus; a claus being the entropy which incurs a waste of 1 joule at a lowest available temperature of unity; *e.g.*, if the lowest available temperature is 200 absolute, and the entropy 10, the incurred waste is 2,000 joules.

Conclusion.—Enough has now been said to show the importance of making an inherently difficult subject as easy to understand as possible; and it is hoped that the somewhat novel way of arranging and treating the subject-matter of the groundwork of thermodynamics may meet with the approval of those who specially deal with that science.

INDEX.

	PAGE		PAGE
ADIABATIC Curve ...	54	Kelvin	58
Board of Trade Unit ...	58	van Laar	131
British Thermal Unit ...	58	Latent Heat ...	67, 115
Carnot	114	Localisation of Entropy ...	28
„ Cycle	14	Lost Work	85
Claus	104, 137	Massieu	71, 122
Clausius	25, 61, 114	Maxwell	7, 61
Compensated Entropy ...	9	Peabody	61
Degradation of Energy ...	6	Perpetual Motion... ..	11, 124
Dissipation of Energy ...	6	Planck	131
Duhem	70, 131, 133	Rankine	35, 61
Energy, Free	133	Rayleigh	122
Entrop	104	Reeve	61
Entropy, Definition 8, 34,	125	Reversibility	26
„ Factor of In-		Sankey	59
curred Waste... ..	22	Second-class Perpetual Mo-	
„ Localisation of... ..	28	tion	12
„ Movement of	94	Second Law of Thermo-	
not a Factor of		dynamics	13
Heat	7	Sensible Heat	115
„ Specific	29	Specific Entropy	29
Equilibrium	130	„ Heat	58, 67
Factors of Heat	67, 134	Stabilities	133
First Law of Thermo-		Thermodynamic Function 35	
dynamics	13	„ Potential... ..	71, 131
Free Energy	133	Thermodynamics, Laws of 13	
Gibbs	61, 71, 122, 133	Third Law of Thermo-	
Heat, Definition	124	dynamics	13
„ Diagram	8, 73	Turbine	91
„ Factors of	67, 134	Uncompensated Work 70, 131	
Heat-Weight	2	Ungained Work	70, 85
Helmholtz	71, 122	Waste	7, 52, 125
Horstmann... ..	122	Watt and State Diagrams 49	
Incurred Waste	22, 52	Work	6
Irreversible Expansion ...	42	„ Lost	85
Isentropic	55	„ Ungained	70

